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A COURSE IN

QUANTITATIVE CHEMICAL ANALYSIS

GRAVIMETRIC AND VOLUMETRIC

BY

NICHOLAS KNIGHT, A.M., PH.D.

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PREFACE.

In the following pages methods for complete analyses are outlined, and substances have been selected for analysis which, it is believed, will illustrate the more common methods of separating and determining the parts of a compound or mixtures of compounds. In some determinations, two or more methods are outlined. In other cases, even though only one process is suggested, it should be borne in mind that there is often a choice of several methods, and the same result can often be attained in many different ways.

The larger works should be freely consulted by the student that he may become acquainted with the variety of processes that are more or less in common use. The work is graduated, and both in the gravimetric and volumetric divisions proceeds from simpler substances and operations to the more complex. The arrangement is such that any part may be omitted to suit the time and convenience of the student.

The ionic theory is now quite generally employed to explain chemical reactions. The theory is usually studied in the courses in general chemistry, and it has not been deemed necessary to introduce the subject here.

Nicholas Knight.

Cornell College,
June, 1915.

CONTENTS.

PAGE
PREFACE iii

PART I

INTRODUCTION 3
The Care of the Balance 3
Weighing 4
Precipitates 5
Filtering and Washing 6
Preparing the Crucibles 8
Desiccators 10
Evaporation 11
The Care of Platinum 11
Distilled Water 12
Cleanliness and Carefulness. Records . . . 12

PART II

GRAVIMETRIC ANALYSIS 17
Filter Papers 17
I. To Analyze a Silver Coin 18
II. Potassium Bichromate 22

PAGE
III. Magnesium Sulphate 24
IV. Copper Sulphate 27
V. Barium Chloride 28
VI. Iceland Spar 28
VII. Dolomite 32
VIII. Siderite 36
IX. Chalcopyrite 41
X. Sodium Phosphate 46
XI. German Silver 48
XII. Smaltite 52
XIII. Fahlerz 59
XIV. Phosphorite (Apatite) . . . 66
XV. Granite 72

PART III

VOLUMETRIC ANALYSIS 91
Indicators 91
General Remarks and Suggestions . . 92
Titration with Potassium Permanganate . 94
Titration with Potassium Bichromate . . 102
Titration with Silver Nitrate . . . 103
Alkalimetry 107
Acidimetry 108
Iodimetry 108

PART IV

PAGE
THE ANALYSIS OF ORDINARY DRINKING WATER 119

PART V

APPENDIX 135
Reactions 135
The Weight of a Volume of Gas . . . 144
The Weight of a Litre of Different Gases Under Normal Conditions, and the Densities Referred to Air 145
Tension of Water Vapor 146
International Atomic Weights . . . 147
Index 149

PART I

INTRODUCTION

PART I.

INTRODUCTION.

The Care of the Balance.

The balance should be kept, if possible, in a well-lighted room on the north side of a thick-walled building, where the temperature is constant. It should not rest against an outer wall. The room should be protected from laboratory fumes. The balance support should be firm, to avoid ordinary jars.

The sensitiveness of the balance depends largely upon the sharpness of the knife edge on which the beam rests when swinging. Therefore release and arrest the beam with a slow and steady movement of the hand, as jerky movements injure knife edges. Arrest the beam only when it is in a horizontal position. A balance with agate knife edges and planes is to be preferred.

Do not allow the pans to rotate in a horizontal direction. This causes a knife edge to scrape on its support.

Arrest both beam and pans before placing anything on the pans or removing anything from them.

A small dish of calcium chloride should remain in the balance case to dry the air.

Weighing.

Sit directly in front of the centre of the balance to avoid parallax.

Carefully remove the dust from the pans with a camel's-hair brush before beginning to weigh.

See that the balance is level. Determine the zero point by observing the swings of the pointer. If adjustment is necessary call on the one in charge of the laboratory.

Place the object to be weighed in the centre of the left-hand pan and the larger weights in the centre of the right. The tenths and hundredths follow in separate rows in the order in which they are taken from their positions.

Weighings should be made with the balance case closed.

Hot objects cannot be correctly weighed, owing to the upward draughts they create about the pans.

Metallic substances should be weighed on a small watch-glass, and no object to be weighed should be placed directly on the scale pan.

Ascertain the weight of the object by the vacant places in the box, and verify when the weights are returned. A neglect of this will often occasion serious error in an analysis.

The most full and clear directions that can be given will not take the place of the competent instructor, who should frequently be consulted by the student, especially in the beginning of the course.

The substance prepared for analysis should usually be contained in a weighing bottle. The bottle and contents together should be carefully weighed, the required amount, generally a gram, withdrawn, and the bottle and contents again weighed. The difference is the amount of the substance taken.

When the weighing is completed do not neglect to close the balance case and to place the cover on the weight box.

Precipitates.

Substances are usually best precipitated in a clean, transparent beaker glass, where the phenomena are more easily observed. The beaker should be covered with a watch-glass when solutions are made and substances precipitated in which there is an evolution of gas. Any accumulations on the watch-glass should be carefully rinsed into the beaker. The size of the beaker should correspond to the amount of the substance it is to contain. (Loss is inevitable from a small solution and precipitate in a large vessel.) Too much of the reagent is to be avoided, as some precipitates are soluble in an excess. To allow certain precipitates to become crystalline, or to collect in aggregates, which renders them less likely to go through the paper, they should stand a number of hours before filtering. In general, the reagent should be slowly added while stirring the contents of the dish, to prevent the carrying down of other substances.

Filtering and Washing.

A filter paper of a size corresponding to the amount of the precipitate should be chosen. The ability to do this can be acquired by a little practice. A paper unnecessarily large requires more wash water, and this involves loss of time in cases where the filtrate must be condensed for subsequent work upon it; besides, as all precipitates are more or less soluble in water, it is on this account desirable to use no more in washing than necessary. If the filter is too large, more of the substance will remain upon it on removal for ignition, which interferes with the success of the work. The paper should be folded to fit perfectly the sides of the funnel, above which it should not project. It should be moistened with distilled water before beginning the filtration. The liquid should first be poured through the paper without stirring up the precipitate from the bottom. By this means the pores are filled, and fine precipitates are not so likely to go through. Grease the edge of the beaker (plain beakers are recommended) with a small quantity of vaseline, and always transfer the substance to the filter by allowing it to flow down a glass rod. The stem of the funnel should touch the side of the receiving vessel to avoid loss by spattering. Substances can be removed from the sides of the containing vessel by a stiff feather properly trimmed, or by a piece of rubber tubing stretched over a glass rod. In filtering, the paper should be filled no nearer the top than four millimetres.

The precipitate can usually be washed with hot water, which more quickly accomplishes the object.* Exceptions are sometimes fine precipitates like barium sulphate, which easily go through the filter, and those soluble in hot water or oxidized by it. Twelve to fifteen washings are generally sufficient, but no rule can be given. A safe way is to test about a cubic centimetre of the filtrate with a suitable reagent, or to evaporate a few drops to dryness on a platinum foil. It is well to collect the washings in a separate beaker, as precipitates will sometimes go through the filter when the wash water is applied.

A vacuum pump can often be employed to advantage in filtering, in which case a platinum cone is necessary for the support of the paper. Care must be exercised that the filter be not ruptured. When the precipitate cracks, it must be pressed together with the glass rod used in filtering to insure thorough washing.

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* The internal friction of water at 100° is less than one-sixth of the friction at 0°.

Preparing the Crucibles.

The crucible, whether of porcelain or platinum, should usually have a capacity of 15^{cc}–20^{cc}. After washing with distilled water, it is heated about ten minutes in the Bunsen flame. The lid should be so adjusted as to cover one-half the mouth of the crucible, which should slant 45° from a vertical position. (Fig. 1.) It should be cooled in the air to about 100°, when it is placed in the desiccator and weighed after about fifteen minutes. It is again heated, cooled, and weighed as before until constant weight is secured, or until two weighings do not vary more than 0.0003 gram. Two crucibles can be heated and cooled at the same time.

Burning the Filter and Heating the Precipitate.

Remove the water from the stem of the funnel with a small strip of filter paper, and cover the mouth of the funnel with a piece of moistened filter paper to protect the precipitate from dust. The precipitate should be thoroughly dried in the air-bath. Meanwhile other work can be in progress, so that time need not be lost. Above a sheet of glazed paper spread upon the table, and held firmly by an iron weight on one corner (light-colored paper for dark precipitates and *vice versa*), remove the precipitate * as thoroughly as possible to a weighed porcelain or platinum crucible, separating adhering particles with a platinum wire. Grasping the crucible with the tongs in the left hand, carefully brush into it any fragments that may have scattered on the

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* Many substances are reduced by the burning paper which are not subsequently oxidized when heated. It is, therefore,

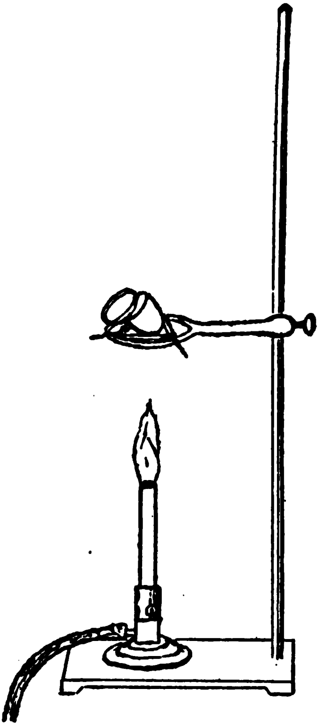

Fig. 1.

desirable to leave as little of the precipitate as possible on the paper, glazed paper. Fold the filter three or four times, wrap it loosely with a piece of platinum wire, ignite the tip with the Bunsen flame, and hold the burning paper just above the crucible. Again, with the camel's-hair brush transfer any residue on the glazed paper to the crucible. Then heat the crucible in the tip of the Bunsen flame, at first carefully and with the cover on, lest any moisture in the precipitate occasion loss. Finally heat to a dull redness * with the cover removed or so placed as to allow a free access of air. Let cool to about 100°. Transfer the crucible to the desiccator, and after standing fifteen to twenty minutes in the balance room it can be weighed. Repeat the heating until constant weight is secured. Deliquescent substances and those that absorb carbon dioxide from the air must be weighed as rapidly as possible. Porcelain crucibles answer for most purposes equally as well as the more expensive platinum. They should be cleaned, heated, and weighed after each analysis.

Desiccators.

There are many convenient forms in common use. The bottom should contain a layer of fused calcium chloride, about an inch in depth. For some purposes, concentrated sulphuric acid or pumice stone saturated with sulphuric acid is a more suitable drying material. The crucible can rest in a pipe-stem triangle.

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* This is ignition or igniting the precipitate.

The desiccators should be kept covered when not in use to prevent the deterioration of the drying agent.

Evaporation.

This usually proceeds in a porcelain dish on the water-bath. During the operation, a funnel should be used to protect the dish and contents from dust. A solution can be quite rapidly concentrated in a flask, inclined at an angle of 45°, heated with a free flame, and sometimes this method can be employed. The flask at the beginning should not be more than half full. Pieces of glass rod, or a small roll of platinum wire, can be inserted in the liquid to avoid bumping. It should be remembered that hot alkalis dissolve the silica of glass, which might interfere with the analyses. Porcelain dishes are less easily attacked than glass.

The Care of Platinum.

In these times when platinum is so expensive, it seems necessary to take every precaution to prolong the life of each article used.

Platinum apparatus should be frequently scoured with fine, moistened sea sand. Heat tends to crystallize the surface of platinum, and the crystalline structure gradually penetrates the dish. Abrading the surface removes the crystals and renders the platinum usable for a longer period.

Liquids containing free chlorine or aqua regia should not be introduced into platinum vessels on account of the solvent action.

Caustic alkalis attack platinum; fusion with these can be made in silver, iron, or nickel dishes.

The shape of platinum vessels should be preserved, and the edges should not be bent.

The stains of iron and other substances can often be removed by placing powdered acid potassium sulphate in the vessel and heating. It should not be so strongly heated as to change all the acid sulphate to the normal sulphate; the latter expands so rapidly that it might break the platinum dish.

Distilled Water.

An abundance of distilled water should be available in all quantitative work. This should occasionally be tested to learn if any residue remains on evaporation. It is frequently stored in glass bottles or carboys, but ordinary glass is appreciably soluble in distilled water. Dishes, before they are used, should be washed with distilled water and it should always be employed in washing precipitates.

Cleanliness and Carefulness. Records.

These conditions are sometimes overlooked, but they are essential to the highest success in this work. Whenever a piece of apparatus has been soiled by use, it should be thoroughly cleaned. Before using, it should be rinsed with distilled water. Apparatus should not be allowed to accumulate on the desk, but should be returned to its appropriate place. The desk should always be scrupulously clean.

The utmost care should be exercised in all details of the work. The student must be constantly on the alert to avoid everything that would mar his results. The habits that can thus be acquired are invaluable. Before beginning an analysis, the general method should be well in mind. It is only in this way that the time can be well filled up and many mistakes avoided. The reason for each step should be clearly in the mind before taking it.

An analysis, or a portion of it, should be repeated if a correct result is not gained. This should always be done when the source of the error has escaped observation.

After some practice, two analyses can be carried on at the same time. Everything should be accurately labelled to avoid mistakes.

The student should form the habit of keeping a neat and business-like record of everything done. Two note-books should be employed,—one to be kept in the laboratory for the daily records; the other to be written up more leisurely. Mistakes made and difficulties encountered should be carefully recorded. All weights should be entered in the note-book and never on loose sheets of paper.

PART II

GRAVIMETRIC ANALYSIS

PART II.

GRAVIMETRIC ANALYSIS.

GRAVIMETRIC chemical analysis consists in separating a compound into elements, or precipitating from the compound in solution other compounds of known composition, and determining the weights of the elements and compounds thus separated. From the weights obtained, the percentage of the different parts of the original compound can be computed. Water of crystallization is usually determined by heating a weighed portion of the substance to constant weight. From the loss in weight, the percentage of water can be determined.

Filter Papers.

Prepared filters, the weight of whose ashes has been determined, can be obtained of the dealers. They can also be prepared from ordinary filter paper as follows: Use five round pieces of sheet zinc with a diameter of 5, 6, 8, 9, and 10^{cm} as models. Cut a number of papers from each model. To remove the inorganic matter from the paper, soak for twenty-four hours in dilute nitric acid (one part acid to ten of water), and wash for the same length of time in a stream of running water. Finally, wash six or eight times in distilled water, thoroughly draining off the water each time. Place these between sheets of filter paper and allow them to dry in a steam-bath for two or three days. They are conveniently kept in round boxes of suitable size.

Ignite ten filters of each size, one at a time, selected from different places in the pile, wrapping each loosely with a piece of platinum wire. Collect the ashes of each ten in a weighed porcelain crucible, heat to dull redness, cool in the desiccator, and weigh. Thus the weight of a filter ash is determined, which must always be deducted from the weight of the precipitate.

I. To Analyze a Silver Coin.

Composition: silver, copper, and tin.

Carefully clean with a little moist sea-sand a five-cent silver coin or the half of a ten-cent coin. Weigh on a watch-glass, transfer to a small beaker, and add two parts of distilled water and one of pure nitric acid. There should be about 50^{cc} of the liquid. Cover with a watch-glass, and dissolve by gently heating with a small flame.*

The tin, which is sometimes present in the coin as an impurity in the copper, separates as a few dark scales of $Sn(OH)_4$ * on the bottom of the beaker. Rinse the accumulations on the watch-glass into the beaker.

---

* The student should write all the reactions that occur in the analyses.

1. TIN—Filter the solution to collect the tin. Wash the precipitate thoroughly with hot water. Remove the precipitate with the filter ashes to a weighed porcelain crucible, and heat to redness until constant weight is secured. $Sn(OH)_4 = SnO_2 + 2H_2O$. From the amount of tin oxide the percentage of tin can be determined.

2. SILVER—Gently heat the filtrate from 1 to boiling. Then with constant stirring cautiously add dilute hydrochloric acid † until no further precipitation takes place. Press the precipitate with a glass rod to expel the liquid from it. Filter, and wash with hot water.

3. The excess of HCl that was added to 2 dissolves a small quantity of silver chloride. Therefore evaporate the filtrate from 2 to dryness on the water-bath, add a few drops of dilute nitric acid, ‡ a little water, and a few drops of dilute hydrochloric acid. Filter, and wash the precipitate with hot water.

4. COPPER—Warm the filtrate from 3 in a porcelain dish on the water-bath. Add a strong solution of caustic potash to slight alkalinity. Let stand for ten minutes on the water-bath and filter with the

---

* Chemically pure copper can be obtained only by electrolysis.

† One part concentrated HCl and one part water.

‡ One part HNO_3 and one part water.

pump. The black precipitate is cupric oxide (CuO). Test the filtrate with a few drops of yellow ammonium sulphide to learn if the copper is all precipitated. Wash the precipitate with hot water until there is no longer an alkaline reaction. Treat the precipitate in the usual way. From the cupric oxide determine the amount of copper.

To determine the percentage of silver:

1. Remove the precipitates from the filter papers to a weighed porcelain crucible. Heat gently until the silver chloride begins to melt. Cool, and transfer to the desiccator.*

2. Weigh a crucible and a piece of platinum wire together, then burn the two filter papers from the preceding operation. The burning paper reduces the small amount of silver chloride to metallic silver.† Some silver will also form an alloy with the platinum. The silver thus obtained added to the amount in the chloride is the total silver in the coin.

To prepare the caustic potash for use in these analyses: To 700^{cc} of absolute alcohol in a glass-stoppered bottle, add 250^{g} commercial caustic potash. Shake the bottle until all the solid has dissolved. Filter the solution into a silver dish. Evaporate the filtrate with the free flame cautiously, lest the alcohol take fire. Toward the end of the evaporation, a dark scum collects on top. This is aldehyde resin. It is produced by the action of the hot alkali on aldehyde, a little of the latter being formed by the oxidation of the alcohol. Remove the scum with a silver spoon and continue the evaporation until a drop of the liquid placed upon a porcelain plate instantly hardens and becomes white and opaque. Place the silver dish in a vessel of cold water until the substance hardens. Remove the cake, place it between filter papers, break it into small pieces with a mallet, and put away in a well-corked bottle.

---

* Finally, remove the chloride from the crucible by adding zinc and dilute hydrochloric acid.

† $4AgCl + \underbrace{C + 2H_2O}_{\text{Paper}} = 4Ag + CO_2 + 4\,HCl.$

The analysis of a silver coin resulted:

Silver	90.52%
Copper	9.40
Tin	0.06
Total	99.98

Remarks.

1. The ashes of the filter papers from the silver chloride may be collected in a separate, weighed crucible, and the metallic silver changed to silver chloride. The platinum wire is wound around the tip of the filter papers, or where there is the least amount of adhering chloride. The residue is moistened with a few drops of nitric acid, and then with a few drops of hydrochloric acid. The substance is

then evaporated to dryness and ignited with the Bunsen burner to expel any moisture. It is then weighed as silver chloride and the amount is added to the main portion.

2. The silver chloride or any silver halide, and many other precipitates may be collected in a weighed Gooch crucible, and the moist precipitate heated as usual. The Gooch crucible may be of porcelain or platinum. It is a crucible of the ordinary size, with a perforated bottom, which should be covered with a layer 2^{mm} thick, of fine asbestos. The asbestos should first be boiled in dilute hydrochloric acid and afterwards well washed in distilled water.

II. Potassium Bichromate.

Composition: $K_2O(CrO_3)_2$.

Weigh four grams of the pure, finely pulverized substance in a small porcelain evaporating dish. With a small flame heat the powder without melting it, constantly stirring with a glass rod, to expel all the moisture. This is accomplished when the powder no longer adheres to the rod.

Transfer the dry bichromate to a clean, dry weighing bottle or test-tube. Weigh a gram into a flask of 200^{cc} capacity, to which add 50^{cc} of dilute hydrochloric acid. Place a small funnel in the mouth of the flask, incline the flask at an angle of 45°, and heat with a small flame until about half the liquid has evaporated. This treatment changes the original substance into potassium and chromic chlorides and a bright green color is obtained.

Transfer the chlorides to a porcelain evaporating dish, warm on the water-bath, and add ammonia to slight alkalinity. This forms chromic hydrate. Continue to heat on the water-bath until all ammonia has been driven off,* adding distilled water from time to time if necessary.

1. CrO_3—Filter with the pump. Wash with hot water. Remove the precipitate from the paper to a weighed porcelain crucible, burn the paper, add the ashes to the crucible, which is heated to dull redness, until constant weight is attained. This gives Cr_2O_3, from which CrO_3 is easily determined.

2. K_2O—Evaporate the filtrate from 1 in a platinum evaporating dish to dryness on the water-bath. Remove the dish, and heat with a Bunsen flame, beginning at the rim and gradually heating toward the bottom to drive off all the ammonium chloride. It can be heated to dull redness without volatilizing the potassium chloride. A black residue will sometimes appear in the dish. This is organic impurity contained in ammonia, and it must be removed. Dissolve the substance in a very small quantity of warm water, stirring with the finger. Filter through a small paper into a weighed platinum crucible. Wash well with hot water and evaporate to dryness on the

---

* Chromic hydroxide is somewhat soluble in dilute ammonia.

water-bath. Heat the crucible to dull redness, cool, and weigh as usual. From the amount of potassium chloride obtained, the percentage of K_2O can be computed.

An analysis resulted:

K_2O	31.63%
$(CrO_3)_2$	68.01
Total	99.64

III. Magnesium Sulphate. $MgSO_4, 7H_2O$.

Pulverize five or six grams of the chemically pure substance and transfer to a weighing bottle. Weigh out three one-gram portions,—one gram in a weighed porcelain crucible for the water determination, one gram in a small beaker for MgO, and one gram in a small beaker for SO_3.

1. To determine the percentage of water:

Place the crucible before mentioned about twenty inches above a very small flame and heat for twenty minutes. Then lower the crucible an inch and leave for seven or eight minutes. Continue lowering an inch and leaving seven or eight minutes each time, until the crucible has nearly reached the flame. Raise the crucible a few inches and cautiously heat with the Bunsen flame. Too great heat would decompose the magnesium sulphate, and the gradual heating is necessary to avoid loss. Cool in the desiccator and weigh as usual. From the decrease in weight the percentage of water can be calculated.

2. MgO—Dissolve the second portion in the beaker with about 100^{cc} of water, add 5^{cc}–10^{cc} of dilute HCl, 25^{cc} of ammonia, and precipitate with a small excess of disodium phosphate solution, with constant stirring. Then add about 25^{cc} of ammonia water, stir vigorously for two or three minutes, let stand for eight hours, and filter. The precipitate is slightly soluble in water, and must be washed in water to which ammonia has been added (one part ammonia water 0.96 spec. grav. and three parts water). The precipitate, magnesium ammonium phosphate, is transferred to a weighed porcelain crucible, to which is added the filter ash. On heating to dull redness, it becomes magnesium pyrophosphate, $Mg_2P_2O_7$, from which the MgO can be computed.

3. SO_3—Dissolve the third portion in about 100^{cc} of water and add 5^{cc}–10^{cc} of HCl. Heat to boiling, and while stirring add a solution of hot barium chloride, drop by drop. Allow the precipitate to settle, add a few drops more of the reagent, and continue until a precipitate ceases to form. Let stand for some hours. Filter, and wash the precipitate with hot water. Heat the precipitate and filter ash in the weighed porcelain crucible to constant weight. From the amount of the $BaSO_4$ obtained the SO_3 can be computed.

An analysis resulted:

H_2O	51.20%
SO_3	32.45
MgO	16.22
Total	99.87

Remarks.

1. Barium sulphate often comes down as a very fine precipitate, and is difficult to filter. By adding hot barium chloride to the hot solution of sulphate, the finer particles are dissolved and add themselves to the coarser particles; also when precipitated hot, there is a tendency for the barium sulphate to crystallize, and therefore, it is less likely to go through the pores of the filter paper. To heat the precipitated substance two or three times to the boiling point, with constant stirring, also increases the size of the particles and makes the filtration an easier process.

2. It sometimes happens that a result too high in magnesia is obtained. This may be due to imperfect washing, or to the formation of another salt $(NH_4)_4Mg(PO_4)_2$, in connection with the ideal phosphate, $MgNH_4PO_4$. Similarly, a high result may be obtained in precipitating phosphoric acid with magnesia mixture. In all cases, the remedy is to dissolve the precipitate in hydrochloric acid, add a *few drops* of the precipitant, disodium phosphate, or magnesia mixture, and ammonia in considerable excess.

Before proceeding with minerals which are more or less complicated in structure, the analysis of two additional simple salts is here suggested. These may be omitted by any who seem to have had sufficient practice from the analyses before indicated.

IV. Copper Sulphate. $CuSO_4, 5H_2O$.

Weigh a gram of the pulverized substance into a weighed porcelain crucible for the water determination, a gram in a porcelain evaporating dish for the CuO, and a gram in a small beaker glass for SO_3.

1. Determine the water by heating the crucible and its contents in an air-bath at 200°–250° to constant weight.
2. The SO_3 is determined as in magnesium sulphate.
3. The CuO is precipitated on the water-bath with a solution of caustic potash, as in the silver coin.

Copper sulphate is frequently associated with ferrous sulphate, from which it can hardly be separated even by repeated crystallization. It can be purified as follows: one hundred grams of the commercial article is dissolved in water and filtered. It is then heated to boiling, and the iron is oxidized with 5^{cc}–10^{cc} of nitric acid. Pure copper sulphate will then crystallize from the concentrated solution. The salt should be thoroughly dried between filter papers and kept in a glass-stoppered bottle.

V. Barium Chloride. $BaCl_2, 2H_2O$.

Weigh a gram of the pulverized salt in a crucible for the water determination, and a gram in each of two small beakers for the barium and chlorine determinations.

1. Determine the water as in magnesium sulphate.

2. BARIUM—Precipitate the hot solution of barium chloride as sulphate with dilute sulphuric acid* from the amount of the barium sulphate, compute the percentage of barium.

3. To determine the chlorine.

Add 5^{cc} nitric acid to the substance in solution and precipitate the chlorine with silver nitrate. Determine similarly to the method employed in estimating the silver of the coin. Do not add the ash from the paper to the precipitate of silver chloride.

VI. Iceland Spar.

Composition: CaO, CO_2, and sometimes SiO_2.

In the analysis of a mineral, about twice as much of the substance should be pulverized as is likely to be required. This amount permits repetition of parts of the work, when necessary. An agate mortar should be used in the preparation of the powder, which should be so fine as not to feel gritty when placed between the teeth. A mineral is frequently not homogeneous, and the powder should be thoroughly mixed before beginning the analysis.

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* One volume of strong acid in six volumes of water.

Select a clear crystal of Iceland spar and pulverize four grams.

1. To determine SiO_2, if present.

Weigh a gram of the powder in a small beaker, add 60^{cc} dilute hydrochloric acid (one part acid, four parts water), covering quickly with a watch-glass. After the substance is dissolved, heat to boiling, and continue the heat for one or two minutes to remove the CO_2. Rinse the watch-glass into the beaker. If SiO_2 is present, after standing a short time, it can be detected with a glass rod as a gritty residue on the bottom of the beaker. Filter, wash with hot water, and transfer to a weighed crucible. Heat, and determine in the usual way.

2. To determine the CaO.

Add ammonia to the filtrate from **1** to slight alkalinity. Heat to boiling, and precipitate the calcium as oxalate with ammonium oxalate. Let stand a few hours and filter.

Transfer the dry precipitate to a weighed platinum crucible and change to calcium sulphate. This is accomplished by adding to the precipitate six or eight drops of conc. sulphuric acid and heating with a Bunsen flame underneath and one above the crucible until fumes of SO_3 no longer escape. Continue the treatment, adding more drops of sulphuric acid, until upon heating constant weight is attained. The percentage of calcium oxide can be determined from the amount of calcium sulphate.

3. To determine the CO_2.

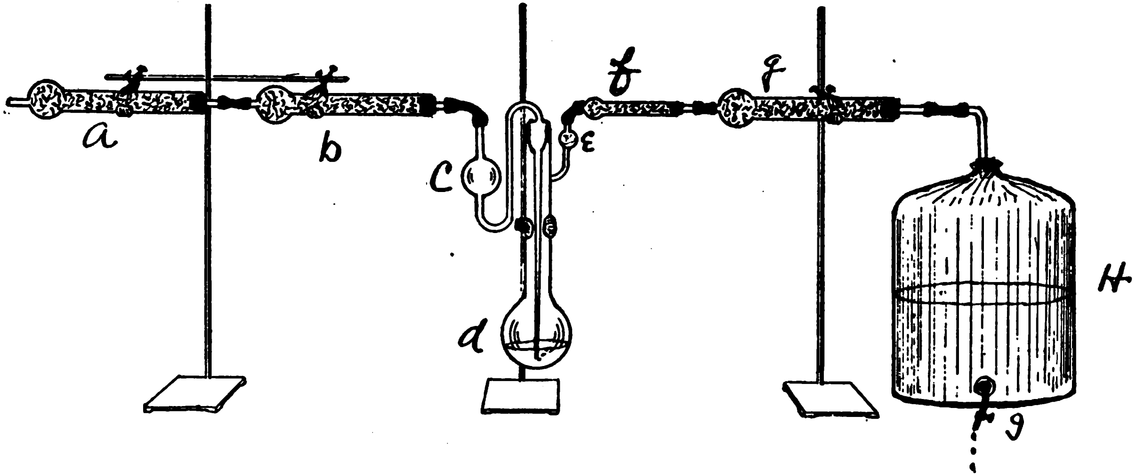

Fig. 2.

Bunsen's method is recommended. (Fig. 2.) The apparatus is inexpensive and can be obtained from the usual dealers. The hydrochloric acid employed in the carbon dioxide determinations should consist of four parts of water to one of strong acid.

A gram of the fine powder is weighed into the flask, d. The bulb, c, is nearly filled with the dilute hydrochloric acid. The bulb, e, contains cotton, which assists in condensing and absorbing the moisture. Attached to the bulb is a small tube, f, filled with fused calcium chloride. The apparatus from c to f, inclusive, is carefully weighed before and after the operation. After the first weighing, with a small rubber tube and the mouth, the acid is brought into d. When effervescence has ceased, the solution is heated to 70° to expel the CO_2. By means of the aspirator, H, air is drawn through the apparatus for fifteen minutes, further to remove the CO_2. The flask, d, is in a beaker of cold water, while the air is aspirated through. It is weighed, heated as before, and air drawn through to constant weight, or until two successive weighings differ by no more than 2^{mg}. From the loss of weight, the percentage may be calculated.

An analysis resulted:

CaO	55.91%
SiO_2	.20
CO_2	43.81
Total	99.92

VII. Dolomite.

Composition: chiefly calcium and magnesium carbonates, with ferrous carbonate, ferric oxide, and silica and sometimes manganese.

1. To determine CO_2.

Proceed as in the case of Iceland spar. When the acid is in contact with the powder it must be slightly warmed to effect solution.

2. SiO_2.

To a gram in a porcelain evaporating dish, add dilute hydrochloric acid and cover with a watch-glass. Warm on the water-bath until all evolution of gas has ceased. Rinse the contents of the watch-glass into the dish and evaporate on the water-bath until crystals begin to appear. Then as the drying continues, stir the substance constantly with a glass rod, until thoroughly dry, and a fine powder remains. Moisten the powder with a few drops of concentrated hydrochloric acid, then with about 20^{cc} of dilute hydrochloric acid and the same quantity of water. Filter while warm. Dry, and ignite the precipitate, which is mainly SiO_2.

3. FeO.*

To the filtrate from 2 add a few drops of fuming nitric acid and heat to boiling to oxidize the iron. Add two grams of ammonium chloride to prevent a precipitation of magnesium. Precipitate the iron with an excess of ammonia.* Filter with the pump and wash with hot water. When heated to a glow the precipitate becomes Fe_2O_3, from which the FeO can be estimated.

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* If manganese is present, the iron and manganese should be determined as in siderite, *q. v.*

4. CaO.

Precipitate the calcium from the preceding filtrate with ammonium oxalate and determine as in Iceland spar.

5. MgO.

Concentrate the filtrate from 4 to a smaller bulk and precipitate with disodium phosphate as in the magnesium sulphate.

The analysis of a rather common specimen resulted as follows:

SiO_2	0.86%
Fe_2O_3	1.14
CaO	30.46
MgO	20.79
CO_2	46.77
Total	100.02

Remarks.

1. The insoluble residue from the hydrochloric acid, chiefly silica, is treated as follows: The residue is ignited in a platinum crucible and

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[*] Such precipitates should not be allowed to stand long, as the ammonia acts upon the glass.

weighed as usual. It is then moistened with a few drops of dilute sulphuric acid, and the crucible nearly filled with a solution of hydrofluoric acid. It is evaporated to dryness on the water-bath, ignited, and weighed. The silica is volatilized by the treatment, and the amount is represented by the loss in weight. The residue, consisting principally of iron and alumina, is removed from the crucible with warm, dilute hydrochloric acid, diluted to a suitable volume, and the small amount of platinum which was dissolved by the hydrofluoric acid is precipitated with hydrogen sulphide. The precipitate is discarded, and after heating the filtrate to remove the excess of hydrogen sulphide, it is added to the main filtrate.

2. Sometimes a second evaporation of the first filtrate will give another residue containing silica, which is to be added to the main portion; and often silica will remain in solution to be precipitated with the iron and alumina (should the latter be present). The dried iron and alumina precipitate is fused with acid potassium sulphate, as in the estimation of titanium oxide, page 72. The fused mass is extracted with water, evaporated nearly to dryness in a porcelain dish, and 25^{cc} concentrated sulphuric acid are added. It is heated with the free flame while copious fumes of SO_3 escape. Water is added to the porcelain dish and the precipitated silica is removed by filtration.

3. Dolomites may also contain alumina, which would be precipitated with the iron. These can al-

ways be separated and determined as described in the analysis of phosphorite, and also as follows: The well-washed, moist precipitate of iron oxide and alumina is dissolved in warm, dilute hydrochloric acid and evaporated in a porcelain dish nearly to dryness to remove most of the hydrochloric acid. An excess of a solution of caustic potash is then added, and it is left fifteen minutes on the water-bath. This precipitates the iron and leaves the alumina in solution as potassium aluminate. Filter and wash the precipitate of iron with hot water. The iron cannot be thoroughly freed from the caustic potash by washing. Therefore, dissolve the moist precipitate of iron with warm, dilute hydrochloric acid, heat to boiling, and precipitate the iron as usual with ammonia. Filter and dry the precipitate, which, on ignition, becomes Fe_2O_3.

Al_2O_3. The first filtrate from the iron is acidified with hydrochloric acid, heated to boiling, and rendered alkaline with a slight excess of ammonia. The ignited precipitate is Al_2O_3.

4. Ammonium chloride prevents the precipitation of magnesium. The ammonia tends to precipitate the magnesium: $MgCl_2 + 2NH_4OH = Mg(OH)_2 + 2NH_4Cl$. But the reaction is reversible, and the tendency is strongly in the reverse direction in presence of an excess of ammonium chloride: $Mg(OH)_2 + 2NH_4Cl = MgCl_2 + 2NH_4OH$.

5. Dolomites and limestones may contain sulphates. These are determined as follows: A portion

of the rock powder is dissolved in hydrochloric acid, and the insoluble portion is removed by filtration. The filtrate is heated to boiling and the sulphate is precipitated with hot barium chloride solution. Insoluble sulphates like barium and strontium sulphates would be contained in the first precipitate, and their determination would require special treatment by fusion in a platinum crucible with sodium carbonate.

6. In precipitating calcium with ammonium oxalate, a small amount of magnesium may also be precipitated as oxalate. To separate these, the precipitate is dissolved in warm, dilute hydrochloric acid, and the solution is rendered alkaline with ammonia. This precipitates the calcium and leaves the magnesium in solution. The filtrate from the calcium is added to the main filtrate containing the greater part of the magnesium, and the whole is precipitated as indicated, with disodium phosphate and a considerable excess of ammonia. When the magnesium content is relatively small the "double precipitation" is not necessary.

VIII. Siderite.

Composition: Principally ferrous carbonate, together with ferric oxide, silica, and manganese, calcium and magnesium carbonates.

1. To determine the CO_2. Proceed as before.

2. To determine the SiO_2. Proceed as with dolomite.

3. To determine the total amount of iron.

To the filtrate from 2, which should be contained in a beaker of 750^{cc} capacity, add drop by drop fuming nitric acid until the dark coloration noticed at first disappears and the solution is yellow. Heat to boiling, and cool in a vessel of water. Add more nitric acid. If there is no change of color, the iron is completely oxidized. Heat to boiling, and neutralize the acids with crystals of sodium carbonate. A watch-glass must be kept on the beaker during the evolution of CO_2 to avoid loss, and the liquid should be heated to the boiling point in the entire process of neutralization. When exactly neutral, precipitate the iron with barium carbonate. An excess of this reagent does no harm. Filter with the pump and wash with hot water.

Then as completely as may be, without injury to the filter, with a trimmed feather transfer the precipitate to the same beaker that was used in the neutralization. Add dilute hydrochloric acid to the precipitate and boil until all is dissolved. The solution now doubtless contains an excess of the acid. Therefore pour the solution through the same filter paper to dissolve the residue upon it. Wash with hot water until the paper is white. Heat the filtrate to boiling and precipitate the barium with dilute sulphuric acid. Let stand twenty-four hours and filter. The precipitate need not be saved. Heat the filtrate to boiling and precipitate the iron with ammonia. Filter with the pump. When ignited, the precipitate becomes Fe_2O_3.

4. After acidifying the filtrate from **3** with hydrochloric acid, concentrate it in a flask. Transfer the substance to a beaker and remove the barium with dilute sulphuric acid.

5. MnO.

Concentrate the filtrate from **4** to 25^{cc}–30^{cc}. Make it alkaline with ammonia and add an excess of yellow ammonium sulphide. Let stand eighteen hours. Filter, and wash the precipitate with cold water that is slightly colored with the ammonium sulphide. Place the filter containing the substance over a porcelain evaporating dish, and using a watch-glass, as there is an evolution of sulphuretted hydrogen, add warm, not hot, dilute hydrochloric acid. Thoroughly wash the filter with hot water.

Leave the filtrate twenty minutes on the water-bath to allow the sulphuretted hydrogen to pass off. Should sulphur separate out, which sometimes happens, filter to remove it. Precipitate with sodium carbonate to alkaline reaction. Let remain fifteen minutes on the water-bath to remove the carbon dioxide. Filter with the pump. When strongly heated, the precipitate becomes Mn_3O_4, from which the MnO can be calculated.

6. CaO.

Concentrate the filtrate from **5** on the water-bath and filter to remove any sulphur. Precipitate the calcium as oxalate. As the quantity is usually small, the dried precipitate can be transferred to a weighed platinum crucible and changed to calcium oxide with a Bunsen flame, or blast lamp.

7. To determine the MgO.

Treat the filtrate from **6** as in previous cases.

8. To determine Fe_2O_3.*

Provide a small flask with a rubber stopper and bulb tube. The upper end of the tube should be closed with a rubber tube and glass plug. With a sharp knife cut a slit about a half-inch long in the rubber tube. This serves as a valve to let the gas escape, but allows no air to enter.† Weigh a portion of the substance into this flask, to which add a small quantity of dilute hydrochloric acid. Dissolve the powder by gently warming. When effervescence ceases, add one or two small crystals of sodium carbonate to create an atmosphere of carbon dioxide. Cool, and precipitate with an excess of barium carbonate. Filter as rapidly as possible with the pump, wash thoroughly in cold water, and discard the filtrate. Dissolve the precipitate in warm, dilute hydrochloric acid, remove the barium with dilute sulphuric acid, and determine the iron as in **3**. Subtract the percentage of iron here obtained, which is the percentage of ferric oxide sought, from the total percentage obtained in **3**. Reduce the difference to FeO, which is the percentage of ferrous oxide sought.

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* The method of Berzelius as improved by Bunsen.

† It is known as the Bunsen valve.

Remarks.

The basic acetate method of precipitating iron and alumina.

This method is applicable when manganese is present as in dolomite and siderite, and further in German silver, smaltite, fahlerz, and granite.

The acid filtrate from the silica is diluted quite largely with water. A solution of ammonium carbonate is gradually added, and with constant stirring until the precipitate, which forms at first, is dissolved with difficulty. In the case of siderite, the solution will now be deep brown in color. The addition of ammonium carbonate is continued until a very slight precipitate forms, which almost disappears when the liquid is stirred, the solution remaining slightly opalescent. A little acetic acid and a moderate quantity of a strong solution of ammonium acetate are added, and boiled for some time. It is filtered while hot, and the precipitate is washed with boiling water. The filtrate and washings must be clear and colorless.

To separate the manganese, which may have been precipitated with the iron and alumina, the precipitate is dissolved in warm hydrochloric acid and treated as before—with ammonium carbonate, acetic acid, and ammonium acetate. The precipitate consists of the iron and alumina as basic acetates, and they can be separated and determined in the usual way.

IX. Chalcopyrite.

Composition: Copper, iron, and lead sulphides; calcium and magnesium carbonates and silica.

1. To determine the sulphur:

In a hard glass tube, 40^{cm} long and 15^{mm} internal diameter, closed at one end, place a layer of well-dried red oxide of mercury,* about 6^{cm} deep; then 12^{cm} of a mixture of equal parts by weight of the mercuric oxide and dry sodium carbonate.† Now add a gram of the powdered chalcopyrite, and lastly 12^{cm} of the mixture before described. With a smooth corkscrew copper wire thoroughly mix the substances down to the layer of mercuric oxide, being careful not to disturb it. Wash the corkscrew wire with a little of the mixture. By gentle rapping, jar the contents of the tube until a small space is formed running its entire length. This allows the escape of gases as the tube is heated.

Place the tube in a combustion furnace and light one burner under the portion of the substance nearest the open end of the tube. At intervals of two or three minutes, light the burners back toward the closed end until all are lighted. Continue the heat until the oxide of mercury has disappeared. Extinguish the burners and allow the apparatus to cool.

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* The oxide is dried in a porcelain evaporating dish with a Bunsen flame. Heat until small globules of mercury adhere to the stirring rod.

† This is dried in the same way as the mercuric oxide. Heat until the vapor of water ceases to come off.

Place the tube on the black glazed paper, and with a file break it into small pieces. Remove these to an evaporating dish, cover with water, and warm thirty minutes. Then with a pair of clean crucible tongs take up each piece of glass and wash the contents into the evaporating dish with hot water. Filter with the pump. The filtrate contains sulphates and sodium carbonate. Add hydrochloric acid until bubbles of carbon dioxide no longer escape. Heat to boiling to remove all the gas. Precipitate the sulphate with barium chloride. Let stand a day before filtering. From the weight of barium sulphate, the percentage of sulphur can be computed.

2. Silica and lead.

Place a gram of the substance in an oxidation crucible of 150^{cc} capacity, and holding a watch-glass in one hand pour on 40^{cc} of fuming nitric acid. Quickly cover the dish with the watch-glass and let stand over night. Still covered, heat the substance carefully on the water-bath until the brown fumes of nitrogen peroxide have all disappeared. Rinse the material on the glass into the dish and evaporate to dryness. When dry add about a teaspoonful of dilute sulphuric acid and evaporate until there is no more odor of nitric acid. Subsequent additions of sulphuric acid may be necessary to accomplish the result.

Transfer the substance to a small beaker and boil. Let stand a few hours and filter off the precipitate, which consists of silica and lead sulphate. Wash eight or ten times with water containing ten or twelve drops of dilute sulphuric acid in 100^{cc} of water, to prevent the solution of the lead. Remove the sulphuric acid from the filter by washing it four or five times in 95 per cent alcohol. Collect the alcoholic filtrate in a separate beaker, and if it is not perfectly clear pass it through the filter again. If clear, throw away.

Dry, heat, and weigh the precipitate. Treat in the crucible with warm nitric acid, which dissolves the lead but does not affect the silica. Decant the solution in a small beaker, and repeat the nitric acid treatment a number of times. Then transfer all from the crucible to the beaker and heat to boiling. Let stand two or three hours and filter the silica, the amount of which is determined in the usual way. Deduct this amount from the weight of both to find the percentage of lead.

3. Copper.

Dilute the filtrate from 2 largely with water,* place it in a beaker which is covered with a perforated watch-glass. Through the watch-glass, pass a stream of sulphuretted hydrogen for about an hour. Filter with the pump, and wash with water to which sufficient sulphuretted hydrogen has been added to render the odor perceptible.†

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[*] CuS is soluble in sulphuric acid unless very dilute.

[†] CuS very easily oxidizes in the air to $CuSO_4$. The sulphuretted hydrogen prevents oxidation.

Dry the precipitate and remove with the filter ashes to a Rose crucible. Prepare a hydrogen apparatus, from which the gas is dried by sulphuric acid and calcium chloride. (Fig. 3.) Heat the crucible to redness without the cover. Add a little sulphur on the point of a knife, turn the stream of dry hydrogen into the crucible through a cover having a hole in the centre. Place a small flame under the crucible and continue heating until there is no more odor of sulphur dioxide. Add another small portion of sulphur, and treat with the hydrogen as before, having the flame underneath. When no further odor of sulphur dioxide is perceptible, extinguish the burning hydrogen, remove the flame, and allow the stream of hydrogen to continue until the temperature of the crucible is about 70°. Remove to the desiccator and weigh as usual. Repeat with the sulphur and hydrogen to constant weight. This treatment gives Cu_2S, from which the amount of copper is determined.

4. Iron.

Concentrate the filtrate from **3** in a flask, which also removes the sulphuretted hydrogen. Transfer to a beaker, oxidize the iron with fuming nitric acid, add about two grams of ammonium chloride, and precipitate with ammonia. Determine as in previous cases.

5. CaO.

Concentrate the filtrate from **4** and proceed as usual.

6. MgO.

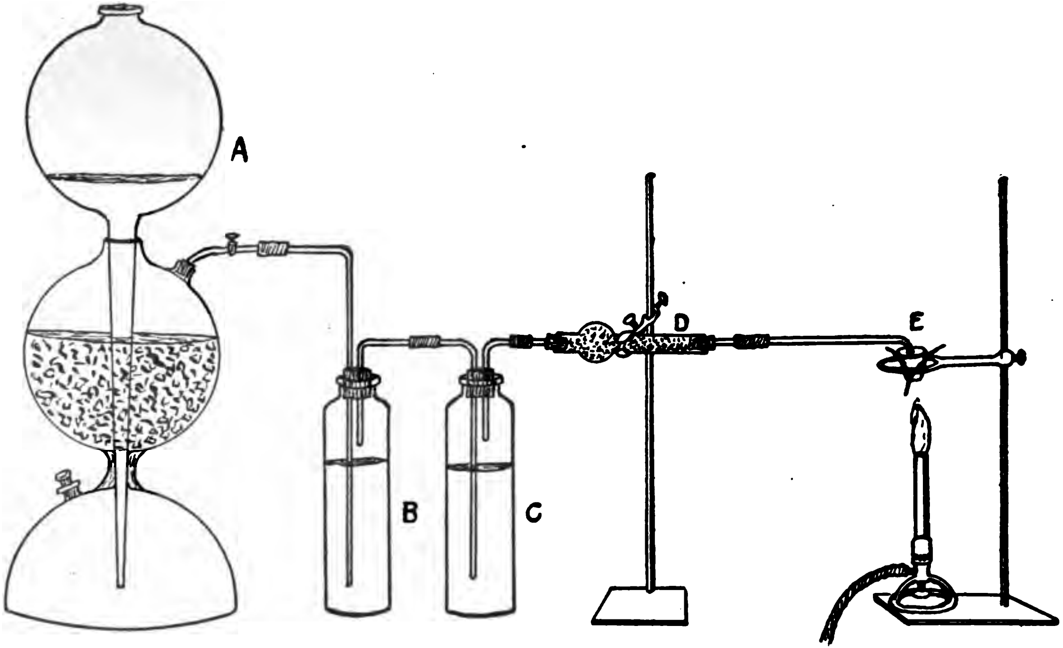

Fig. 3.—A, Kipp apparatus. B, C, wash bottles containing conc. sulphuric acid. D, calcium chloride tube. E, Rose crucible.

Concentrate the filtrate from 5 and proceed as before.

7. CO_2.

The Bunsen method can be used; but in a sulphide like chalcopyrite and smaltite it is necessary to prevent the escape of hydrogen sulphide, as this would give too high a result in CO_2. This is accomplished by the use of dilute sulphuric acid instead of hydrochloric acid. If there is still an odor of hydrogen sulphide, or if lead paper should indicate the formation of the gas, a small quantity of powdered copper sulphate, ferrous sulphate, or potassium dichromate is introduced into the bulb with the powdered mineral or rock, and the determination can proceed as in other cases.

X. Sodium Phosphate. $Na_2HPO_4, 12H_2O$.

1. The acid, P_2O_5.

Weigh a gram of the substance in a small beaker and dissolve it in a little water. In another beaker place a small quantity of magnesium chloride, which should be dissolved in hydrochloric acid. Then add ammonia to alkalinity. If a precipitate forms, it must be dissolved by a little more hydrochloric acid. Let this *magnesia mixture* cool, and with it precipitate the solution of sodium phosphate. Add to the whole one-third its bulk of ammonia water and let stand some hours before filtering. When heated to redness the substance becomes magnesium pyrophosphate, from which the percentage of P_2O_5 can be computed.

2. The base, Na_2O.

Evaporate the filtrate from 1 to dryness in a platinum dish and drive off the ammonium chloride with the free flame as in determining the base of potassium bichromate. Then add about 200^{cc} of baryta water, again place the dish on the water-bath, and evaporate to dryness. Dissolve the residue in a little water and filter with the pump. The filtrate soon absorbs carbon dioxide from the air, and the barium carbonate thus formed causes a turbidity of the liquid, which is easily removed by a few drops of hydrochloric acid.

Precipitate the barium with the smallest possible excess of dilute sulphuric acid. Filter. Evaporate the filtrate in a platinum dish until there is no further decrease in volume. Then with the direct flame continue the heating to remove the excess of sulphuric acid. The residue still contains barium sulphate. To remove this, dissolve in a little water and filter in a weighed platinum crucible. Evaporate the filtrate to dryness on the water-bath and heat further with the free flame to expel all moisture. The substance is now acid sodium sulphate, and it must be changed to the neutral salt. To accomplish this, add, two or three times, a piece of ammonium carbonate as large as a pea, and heat the crucible to redness after each addition. Repeat to constant weight.

3. Water.

Place a gram of the substance in a weighed porcelain crucible and heat in an air-bath at 300° to constant weight.

An analysis resulted:

H_2O	62.84%
P_2O_5	19.83
Na_2O	17.31
Total	99.98

XI. German Silver.

Composition: Copper, zinc, and nickel, together with small quantities of tin, lead, and iron as impurities.

Clean about a gram of the alloy by the use of sea-sand and water.

1. To determine the tin.

Dissolve the substance in a small beaker by gently heating, covered, with 50^{cc} of dilute nitric acid. A small precipitate of tin hydrate may appear, and should be treated as in the analysis of the silver coin.

2. To determine the lead.*

Evaporate the filtrate from 1 in a porcelain dish to dryness on the water-bath. Add 10^{cc} of dilute sulphuric acid and continue the evaporation until there is no odor of nitric acid. It may be necessary to add several portions of the acid. Dissolve the residue in a little water, transfer to a small beaker, and heat to boiling. Let stand some hours, and filter and wash as in the analysis of chalcopyrite.

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* If a qualitative analysis does not disclose the presence of lead, determine the copper at this stage.

3. To determine the copper.

Dilute the filtrate from **2** largely with water and introduce a stream of sulphuretted hydrogen. This precipitates the copper and some zinc. To remove the zinc wash the precipitate four or five times with water containing sulphuretted hydrogen, to which has been added one-third of its bulk of dilute hydrochloric acid. Remove the acid on the filter by washing six or seven times with water containing a little sulphuretted hydrogen.

Transfer the filtrate as quickly as possible to a large flask and heat to expel the sulphuretted hydrogen. Continue the heating until a small bulk is reached. Determine the copper in a Rose crucible as in chalcopyrite. (Fig. 3.)

4. To determine the iron.

The filtrate from **3** cannot be treated with ammonia, as it would precipitate some nickel. It is oxidized with a few drops of nitric acid, heated to boiling, and kept at that temperature while neutralized with sodium carbonate, as in siderite. Toward the end of the operation, it is better to add a *solution* of sodium carbonate to secure an exact neutralization. The iron is then precipitated with about 10^{cc} of sodium succinate *solution*. Filter with the pump and wash with cold water. The iron present is small, and appears as a coloration on the filter paper. It becomes Fe_2O_3 on heating to redness in the crucible.

5. To determine the zinc.

Evaporate the filtrate from **4** to a convenient volume, and while still on the water-bath add a solution of sodium carbonate. This precipitates both zinc and nickel as carbonates. Let remain a half-hour on the water-bath to expel the carbon dioxide. Filter with the pump and wash with hot water.

With a feather and the free use of water, transfer the precipitate to a porcelain evaporating dish, saving the filter on account of the small quantity of precipitate that remains upon it. Place the substance upon the water-bath, concentrate to a smaller bulk if necessary, and add small amounts of hydrocyanic acid and caustic potash solution until the green carbonates give place to a substance of uniform whiteness. The two reagents employed form potassium cyanide. While adding them, a watch-glass must cover the dish, as there is an evolution of carbon dioxide. Continue to heat on the water-bath until all carbon dioxide has passed away. To secure the white appearance it may be necessary to add two or three portions of the hydrocyanic acid and caustic potash. Finally, evaporate the solution to a small bulk.

The precipitate is nickel paracyanide, which has been formed in the operation. Filter through the paper that contained the nickel and zinc carbonates and dry the precipitate.

The warm filtrate in a porcelain dish on the water-bath should be precipitated with potassium sulphide.* Filter and wash the precipitate with water containing a little of the reagent, to prevent the oxidation of the zinc sulphide.

Dissolve the precipitate on the filter with warm dilute hydrochloric acid. Evaporate the zinc chloride to a convenient size, and then filter into an evaporating dish to remove the sulphur. Place the dish on the water-bath, and covering with a watch-glass, precipitate the zinc with a small excess of sodium carbonate. Let the substance stand a few minutes on the water-bath and filter with the pump. The zinc carbonate when heated to constant weight becomes zinc oxide.

6. To determine the nickel.

Evaporate the filtrate from **5** to dryness, and having the dish covered with a watch-glass add hydrochloric acid, stirring with a glass rod. Evaporate again to dryness and then add *aqua regia.*† This destroys the organic matter, and the green color should appear at least after two or three additions of the reagent. The yellow coloration is due to nickel paracyanide. Evaporate to dryness and add to the residue about 50^{cc} water. Filter, wash, and dry the precipitate.

There are now two filters containing nickel paracyanide. Ignite them in a porcelain crucible and dissolve the nickel in a little dilute hydrochloric acid. Remove the silica which the alkalis have dissolved from the porcelain, and the ashes, by filtering. Add this filtrate to the main portion of the nickel,—the filtrate from the second portion of nickel paracyanide,—and precipitate as hydrate with a concentrated solution of caustic potash. When heated to redness this becomes nickel oxide,* NiO.

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* This is made by taking equal weights or volumes of a solution of caustic potash, saturating one portion with hydrogen sulphide, and pouring into this the other portion.

† 3 parts HCl and 1 part HNO_3.

An analysis resulted:

Ni	15.39%
Zn	22.18
Cu	62.30
Pb	.13
Fe	.11
Total	100.11

XII. Smaltite.

Composition: Cobalt arsenide or cobalt-nickel arsenide, together with sulphur, silica, zinc, iron, copper, bismuth, lead, calcium, magnesium, and carbon dioxide.

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* The precipitate of nickel hydroxide should be washed fifty or sixty times with boiling water, until the washings give no cloudiness with a solution of silver nitrate. After the precipitate is ignited, it may be necessary to wash the nickel oxide again with boiling water.

A. 1. To determine the CO_2.

Proceed as in previous cases.

2. To determine the sulphur.

Place a gram of the powdered mineral in an oxidation crucible and add 50^{cc} of dilute nitric acid. Cover with a watch-glass and heat on the water-bath until the evolution of gas ceases. Rinse the contents of the watch-glass into the crucible and evaporate to dryness. Then add successive portions of dilute hydrochloric acid, evaporating each time to dryness until no more odor of nitric acid can be observed. Transfer the substance to a small beaker, boil upon the addition of water, and after standing some hours filter.

The precipitate contains silica and lead sulphate. Place the paper in a small beaker, add dilute hydrochloric acid, and boil to dissolve the lead sulphate. Filter into the preceding filtrate. Dilute the filtrates with water, heat to boiling, and precipitate with barium chloride. Let stand a day and filter. From the amount of the barium sulphate compute the percentage of sulphur.

B. To determine the bases and silica.

1. Lead and silica.

Place a gram of the substance in an oxidation crucible and add nitric acid, as in the determination of sulphur. Remove the nitric acid with sulphuric acid. Transfer to a small beaker and heat to boiling. Filter. The precipitate contains silica and lead sulphate, which are treated as in chalcopyrite.

2. To determine the arsenic.

Dilute the filtrate from **1** to a volume of 200^{cc} and heat to 60°–70°. This temperature must be maintained from three to six hours, while a stream of sulphuretted hydrogen is run through the liquid. The loss by evaporation must be supplied. This precipitates arsenic, bismuth, and copper, while the other substances remain in solution. Filter with the pump and wash well with cold water. Remove the precipitate to the same beaker and warm with potassium sulphide. This dissolves sulphides of arsenic, but does not change the copper and bismuth sulphides. Now filter through the paper from which the precipitate was removed. Wash in cold water, dry, and keep for future work upon it.

Evaporate the original filtrate from the sulphides to a smaller volume, heat to 60°–70°, and again pass through the liquid a stream of sulphuretted hydrogen. In case the arsenic, bismuth, and copper were not all precipitated the first time, more will be thrown down. This must be treated with potassium sulphide as before. Filter off the copper and bismuth and dry.

Evaporate the solutions of arsenic to dryness on the water-bath. If sulphides of bismuth and copper separate from the solution, as is quite likely, filter, and keep the precipitate with the other two portions.

Transfer the arsenical residue to an oxidation crucible, using as small a quantity of water as possible. Add about seven grams of solid caustic potash, which the water should dissolve. Then for about twenty minutes pass a stream of chlorine free from air into the crucible, which is kept warm on the water-bath. The gas has run sufficiently long when the substance bleaches litmus paper. It is necessary to have a wash bottle at hand, as the potassium chlorate which forms may clog the delivery tube.

With the crucible covered by a watch-glass, add about 50^{cc} of dilute hydrochloric acid to decompose the potassium chlorate which has formed. Evaporate on the water-bath until crystals appear. Then repeat the operation, using 50^{cc} of concentrated hydrochloric acid.

By the use of hot water, transfer the contents of the crucible to a beaker glass and filter to remove the sulphur and silica. If, upon the paper, yellow flakes of arsenic sulphide appear, they must again be transferred to the oxidation crucible, and the treatment with caustic potash, chlorine, and hydrochloric acid repeated. Finally filter off the silica and sulphur. The two filtrates containing arsenic are now united and kept three to six hours at 60°–70° while a stream of sulphuretted hydrogen is run through. The precipitate is As_2S_5.

The sulphides of arsenic cannot be strongly heated on account of their volatility. They are determined as follows: A filter paper on a watch-glass is heated for three hours in a thermostat at 105°–110°. It is transferred to a weighing bottle, and its weight determined. Return it to the thermostat for half an hour and again weigh, repeating if necessary until constant weight is attained.

The arsenic is filtered through this paper, washed with cold water, and then with alcohol three or four times to convert the amorphous into crystalline sulphur, which is soluble in carbon disulphide; then four or five times with carbon disulphide, and again with alcohol. Place in the thermostat and heat (cautiously at first, lest the alcohol take fire) to 105°–110° to constant weight. The substance and paper are weighed each time in the weighing bottle. From the amount of sulphide, the percentage of arsenic can be computed.

3. To determine the iron.

The filtrate from the sulphides of arsenic, bismuth, and copper is placed in a beaker, covered with a watch-glass, and heated to remove the hydrogen sulphide. It is oxidized with fuming nitric acid. Heat the solution to boiling and neutralize with crystals of sodium carbonate. Precipitate the cool solution with sodium succinate.

4. To determine the nickel. Liebig's method.

The filtrate from **3** is evaporated in a porcelain dish to a small volume. If more iron separates out, filter. If the solution remains clear, add a solution of caustic potash to the substance on the water-bath, which precipitates the nickel and cobalt as hydrates, $Ni(OH)_2$ and $Co(OH)_2$.

Let remain about twenty minutes on the water-bath, until the hydrates become a dirty bluish-green color. Filter with the pump and wash with hot water. The precipitate is removed from the paper with a feather to an evaporating dish, and hydrocyanic acid is added until a reddish tint, not very pronounced, is assumed; then a solution of caustic potash drop by drop, until a yellow color appears and all is dissolved save a small yellow flocculent precipitate of cobalt paracyanide, which is formed. Filter with the pump through the paper from which the hydroxides were removed, after moistening the filter with hydrocyanic acid. By the foregoing treatment $K_3Co(CN)_6$ and $Ni(CN)_2$ are formed.

Concentrate the filtrate to a smaller volume, add mercuric oxide suspended in water until the liquid remains a red color. This precipitates the nickel as hydrate, but does not change the cobalt. Let remain about one hour on the water-bath, and while warm filter with the pump, washing the precipitate with hot water. Heat finally with the blast lamp to drive off the excess of mercury.

5. To determine the cobalt.

Place the filtrate from which the nickel was filtered in a platinum evaporating dish and evaporate to dryness. Sulphuric acid acts more readily upon it in this condition. The cobalt paracyanide is united to the main portion. Now add about 30^{cc} dilute sulphuric acid, and after half an hour 20^{cc} of conc. sulphuric acid. As there is an evolution of gas, the dish must be covered with a watch-glass for some time. Evaporate to as small a bulk as possible on the water-bath, and then heat cautiously with the free flame to remove all sulphuric acid. Treat the residue with a little hot water and filter off the mercury salt that it may contain. Wash the precipitate well with hot water and evaporate again to dryness; add a little hot water and again filter, to remove the last trace of mercury, into a porcelain evaporating dish.

Place the filtrate on the water-bath and precipitate while hot with a solution of caustic potash. The substance is a dark color when sufficient of the reagent has been added. Filter the precipitate, wash thoroughly in hot water, dry as usual, and remove to a weighed porcelain crucible. Add a centimetre of water, and test the liquid with strips of red and blue litmus paper. If the reaction is alkaline, the precipitate must be further washed to remove the caustic potash. If it reacts acid, this is due to $CoSO_4$, which has an acid reaction, and more caustic potash must be added to the solution to precipitate all the cobalt. If the reaction is neutral, evaporate to dryness on the water-bath, and heating with a small flame reduce to metallic cobalt with a stream of dry hydrogen gas.

6. To determine the zinc.

Heat the filtrate from **4** to boiling, add a little acetic acid, and for half an hour run a stream of sulphuretted hydrogen through the liquid. Filter and wash the precipitate with water containing a little acetic acid. Treat the dry zinc sulphide in a Rose crucible with hydrogen and sulphur, as in the determination of copper in chalcopyrite.

7. To determine the calcium.

Evaporate the filtrate from **6** to a smaller volume, filter off the sulphur, and proceed as before.

8. To determine the magnesium.

Proceed as before.

9. To determine the bismuth.

Transfer the precipitates of bismuth and copper to a crucible and heat. This changes the sulphides to oxides. Dissolve the oxides in warm nitric acid and filter. Wash the paper with hot water which contains a little nitric acid to prevent the precipitation of bismuthyl nitrate ($BiONO_3$). Add ammonia to the filtrate on the water-bath, which precipitates the bismuth as hydrate $Bi(OH)_3$.

10. To determine the copper.

Precipitate the filtrate from **9** with sulphuretted hydrogen and determine as in previous cases

XIII. Fahlerz.

Composition: Copper, arsenic, and antimony sulphides. It may also contain water, mercury, silver, iron, silica, zinc, cobalt, nickel, manganese, lead, calcium and magnesium carbonates.

Ten grams should be pulverized, as five portions are necessary: one for the sulphur determination, one for carbon dioxide, one for water, one for mercury, and one for the other bases.

A. 1. To determine the CO_2.

Proceed as in previous cases.

2. To determine the sulphur.

Use the combustion furnace as in chalcopyrite.

B. To determine the bases and silica.

1. Antimony.

Place a portion of the substance in a platinum crucible, nearly fill the crucible with freshly prepared potassium sulphide, and let it remain fifteen minutes on the water-bath, stirring occasionally with a platinum spatula. Decant the clear liquid into a two-litre beaker and repeat the treatment with potassium sulphide six or seven times. Then pour the contents of the crucible into the beaker, washing the crucible as well as possible. Some of the sulphides will cling to the walls, but no attention is paid to this until later, when it is dissolved in nitric acid and added to the remainder of the sulphides treated with the same reagent.

Add a litre and a half of water to the beaker, stir thoroughly with a glass rod for ten minutes, and let stand over night. The arsenic and antimony are in solution, while the remaining sulphides are undissolved. Filter with the pump and wash with cold water. (Hot water usually causes sulphides to oxidize.) Dry the precipitate and remove with the filter ashes to the oxidation crucible.

Dissolve the sulphides remaining on the platinum crucible with fuming nitric acid, place this also in the oxidation crucible with more nitric acid to oxidize the sulphides to sulphates. Let stand three or four hours and evaporate to dryness. Add a little water and *exactly* neutralize with a solution of caustic potash. Exact neutralization at this stage is highly important.* Then add 50^{cc} potassium sulphide in successive portions to extract the remainder of the arsenic and antimony. Decant into a large beaker, adding finally the undissolved residue. Dilute largely with water, let stand over night, and filter in the morning.

The filtrates from both extractions are united and strongly acidified with sulphuric acid. This precipitates the arsenic and antimony.

After standing twenty-four hours, filter with a pump, and with a feather transfer the precipitate to a porcelain evaporating dish. Add a dilute solution of caustic potash and leave on the water-bath until all is dissolved. Concentrate the solution, and filter if there is a separation of copper sulphide. Collect the filtrate in an oxidation crucible and evaporate until there is a layer on the bottom about a centimetre deep.

Add to the crucible about ten grams of solid caustic potash with sufficient water to dissolve it. Then pass through a stream of chlorine, until the substance only bleaches litmus, to oxidize fully the arsenic and antimony. Decompose the potassium chlorate with dilute and concentrated hydrochloric acid, as in smaltite.

Remove the substance from the crucible into a large beaker, add 200^{cc} of strong hydrochloric acid, and then sufficient dilute hydrochloric to dissolve the potassium chloride. Filter off the silica which was dissolved from the crucible, and to the filtrate add 200^{cc} sulphuretted hydrogen water, which precipitates only the antimony. Filter, and by an aspirator or filter pump conduct air through the filtrate for a number of hours to remove the suphuretted hydrogen.

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* If free acid is present, the potassium sulphide is decomposed, and the arsenic and antimony would not be dissolved. If there is an excess of the alkali, some iron might go into solution, which would not be estimated.

Dissolve the antimony on the filter with potassium sulphide into a cleaned, dried, and weighed platinum dish of 100^{cc} capacity. Concentrate the solution until the dish is half full. Place the dish on the negative pole of a Bunsen cell and introduce into the liquid a coil of platinum wire, suspended from the positive pole. Let the electric current pass through eight to twelve hours. To ascertain when all is decomposed, by means of a capillary tube withdraw two or three drops, place in a small watch-glass, and add a drop or two of sulphuric acid. If only a whitish precipitate results, it is sulphur, and the decomposition is complete. Without disturbing the deposit of antimony, pour the liquid from the dish, wash four or five times with water and then with alcohol. Dry in the desiccator and weigh.

2. To determine the arsenic.

The filtrate through which the stream of air has passed is placed in a beaker and precipitated at a temperature of 60°–70° with a stream of sulphuretted hydrogen. It is filtered on a weighed paper and determined as in smaltite.

3. To determine the lead and silica.

The sulphides from which the arsenic and antimony were removed are placed together with the ashes of the filter in an oxidation crucible and treated with fuming nitric acid. Evaporate to dryness and expel the nitric with sulphuric acid. Add 200^{cc} water, heat to boiling, and filter. The precipitate consists of lead, silica, and a little iron.

Dry the precipitate, remove it with the filter ash to a weighed porcelain crucible, heat to redness, and weigh. Treat it with 15^{cc} nitric acid and heat to boiling. Filter, and determine the silica as usual.

Oxidize the filtrate with fuming nitric acid and precipitate the iron with ammonia. Determine the weight of the iron. The amounts of iron and silica now being known, the percentage of lead can be computed.

4. To determine the silver.

To the filtrate from 3 add two or three drops dilute hydrochloric acid. A larger quantity of acid might dissolve the silver chloride which is contained. The small quantity of chloride usually present is reduced to metallic silver by the burning paper.

5. To determine the copper.

Treat the filtrate from 4 with sulphuretted hydrogen. Filter, and wash the precipitate with dilute hydrochloric acid, and then with water containing sulphuretted hydrogen, as in German silver. Add this portion to that which separated out in connection with the antimony determination, and estimate as in previous cases.

6. To determine the main portion of the iron.

Evaporate the filtrate from **5** to a smaller volume to expel the sulphuretted hydrogen. Oxidize with fuming nitric acid, neutralize while hot with sodium carbonate, and precipitate the cold solution with sodium succinate. The iron thus obtained is to be added to that received in connection with the determination of lead and silica.

7. To determine the zinc, nickel, and cobalt.*

Acidify the filtrate from **6** with acetic acid. Heat on the water-bath to boiling to see if more iron will separate out. If not, introduce a stream of sulphuretted hydrogen for half an hour. Wash the precipitate in water containing ammonium acetate. Treat like zinc sulphide in smaltite.

8. To determine manganese, calcium, and magnesium.

These are usually present in small quantities, if at all, and can be estimated together. Evaporate the filtrate from **7** to a volume of 40^{cc}–50^{cc}, and if sulphur appears, filter. Precipitate on the water-bath with sodium carbonate. Dry the precipitate, and determine as usual in a porcelain crucible.

9. To determine the mercury.

The method is similar to that employed in the estimation of sulphur in chalcopyrite. The tube should be about 60^{cm} in length. At the bottom, there should be a layer, 5^{cm} in depth, of manganese carbonate dried with a small flame. Then about 10^{cm} of lead oxide (PbO) thoroughly dried in the same way, followed by a gram of the substance. Again, 10^{cm} of the lead oxide. With a copper spiral, thoroughly mix the substances down to the manganese carbonate, which should not be disturbed.

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* The nickel and cobalt are usually present in such small quantities that they can be estimated with the zinc.

About 10^{cm} of the tube should project out of the combustion furnace, into which portion the vapors of mercury will condense. Ignite the burners slowly to avoid breaking the tube, and heat until lead oxide is melted upon the glass.

With a wet string, break off the portion of the tube which contains the mercury and place it in a desiccator in which sulphuric acid is the dryer. It should remain until all traces of moisture have disappeared. Weigh the tube and mercury. With a strip of paper remove all mercury and weigh again. From the difference in weight, the percentage of mercury can be determined. The lead oxide is used to combine with the substances other than mercury which are volatile.

To determine the water.

A bulb tube of hard glass and three freshly filled calcium chloride tubes are necessary.

Place three to four grams of thoroughly dried lead oxide in the bottom of the bulb, then a gram of the substance, and upon it more lead oxide. Roll the tube until the different layers are well mixed together. Lastly, completely cover the top of the mixture with more lead oxide.

Connect two calcium chloride tubes on one end of the bulb tube, the first having been weighed. Connect an aspirator to the second calcium chloride tube. The third calcium chloride tube connected with a wash bottle containing sulphuric acid is attached to the other end of the bulb tube. While heating the bulb with a Bunsen flame, draw air through the apparatus. The moisture will collect in the weighed tube, and the percentage can be computed.

XIV. Phosphorite (Apatite).

Composition: Mainly calcium phosphate. It also contains magnesia, alumina, silica, iron, chlorine, fluorine, carbon dioxide, and water.

A. 1. To determine the CO_2.

Proceed as in previous cases.

2. To determine the fluorine.

Place two grams of dry sodium carbonate in a platinum crucible, then a gram of the powdered mineral, and three grams of sodium carbonate. Mix well with a platinum wire arranged in the form of a corkscrew. Cover the crucible and heat for ten minutes with a Bunsen flame, and then for half an hour with a blast lamp, until all is fused and no more carbon dioxide escapes.* Cool by blowing air with the bellows against the sides of the crucible.

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* The crucible containing the substance in a state of fusion may be grasped with the tongs and given a rotary motion. This distributes the substance upon the sides of the crucible, by which it may more easily be removed.

Transfer the crucible and its contents to an evaporating dish, cover with water, and heat for half an hour on the water-bath. Filter, and wash with hot water. Fusing with sodium carbonate changes calcium chloride and fluoride to the sodium salts which are in the filtrate.

Place the filtrate in an evaporating dish on the water-bath, and add 15^{cc} of a solution of ammonium carbonate to precipitate the silica. Filter, and wash with hot water.

Again transfer the filtrate to the water-bath and add a little ammonium zinc sulphate.* Evaporate to dryness on the water-bath, stirring with a glass rod to a fine powder. Add hot water and filter with the pump.

Acidify the filtrate with acetic acid, and to it add a solution of calcium chloride as long as a precipitate continues to form, and then a few drops of a solution of sodium carbonate. Heat on the water-bath until crystals appear. Filter, wash, and dry the precipitate. Heat it with the filter ash in a porcelain crucible. Transfer the contents of the crucible to a small evaporating dish and again treat with acetic acid. Filter, dry, and heat the precipitate, which is calcium fluoride, to dull redness. From the amount obtained, the percentage of fluorine can be determined.

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* This is made by dissolving zinc in sulphuric acid, filtering, and adding to the filtrate sufficient ammonia to dissolve the precipitate which forms at first.

3. To determine the chlorine.

A gram of the substance is fused with sodium carbonate and treated with water, as in the case of fluorine. Acidify the filtrate with nitric acid and add a solution of silver nitrate to precipitate the chlorine as silver chloride. Let stand some hours in a dark place and filter. In burning the paper, the chloride is changed to metallic silver, from the weight of which the chlorine is easily determined.

B. To determine the bases, phosphoric acid and silica.

1. Silica.

Place a gram of the substance in a porcelain evaporating dish and add nitric acid, covering with a watch-glass during the evolution of gas. Remove the cover and evaporate to dryness.

When about the consistency of syrup, stir the substance with a glass rod, during the further evaporation, until a fine dry powder results. Then add 50^{cc} nitric acid and about the same quantity of hot water, and leave for fifteen minutes on the water-bath. Filter. The precipitate contains silica and a small quantity of iron. Dry. Heat the precipitate to redness in a porcelain crucible, cool, and weigh.

Treat the precipitate on the water-bath with dilute hydrochloric acid. Let it remain a few moments on the water-bath and decant the clear liquid into a beaker. Repeat this several times until the iron is dissolved. Transfer the residue to the beaker which contains the liquid, heat to boiling, let stand some hours, and filter. Transfer the dried precipitate and filter ash to a weighed porcelain crucible and determine the percentage of silica. Precipitate the iron in the filtrate with ammonia and determine the percentage. This is to be added to another portion determined later.

2. To determine the phosphoric acid, as P_2O_5.

Evaporate the filtrate from 1 almost to dryness, add about 30^{cc} nitric acid, and while covered, add two grams of tin foil in small pieces. The tin unites with the phosphoric acid, forming the phosphate $Sn_3(PO_4)_4$.

When nitrogen peroxide ceases to come off, remove the watch-glass and filter with the pump. By the use of water, remove the precipitate to a porcelain evaporating dish and warm on the water-bath. Then add sufficient solution of caustic potash to dissolve it. Filter through the paper from which the tin was removed, and wash with hot water (save the paper for subsequent treatment, as it may contain iron).

Dilute the filtrate with water to one and a half litres, acidify with sulphuric acid, and run a stream of sulphuretted hydrogen into it for three hours.

Let stand over night and filter. Wash six times with undiluted sulphuretted hydrogen water.

Transfer the filtrate to a large flask and concentrate to a bulk of 100^{cc}–200^{cc}. Again pass through the liquid a stream of sulphuretted hydrogen to precipitate any tin that may have oxidized and gone into solution.

Filter and wash with sulphuretted hydrogen water as before. Evaporate the filtrate to expel sulphuretted hydrogen, oxidize with a few drops of fuming nitric acid, and add ammonia to precipitate the iron, which frequently comes down with tin and is in solution as iron sulphate. The ammonia precipitates the iron as phosphate ($FePO_4$), from the amount of which the Fe_2O_3 and P_2O_5 can be computed. Both are to be added to portions that will be separated later.

The filtrate from the iron phosphate is precipitated with magnesium ammonium chloride, magnesia mixture, prepared as in the analysis of disodium phosphate. The magnesium ammonium phosphate thus formed is treated in the customary way.

3. To determine alumina and the remainder of the iron.

Treat the filtrate from 2 with a current of sulphuretted hydrogen to remove traces of copper, zinc, and lead which are present in tin foil and may still be in solution. Filter with the pump and wash with cold water. Heat the filtrate to boiling to expel the sulphuretted hydrogen. Oxidize with fuming nitric acid and add ammonia to slight alkalinity. Heat again to expel the excess of ammonia. Filter with the pump and wash with hot water. Dry, heat, and weigh the precipitate.

Nearly fill the crucible with dilute hydrochloric acid, let it stand ten minutes on the water-bath, and decant the clear liquid. Repeat until all is dissolved.

Filter to remove the ashes, and collect the solution in a small platinum evaporating dish.

Place the dish on the water-bath, and evaporate to a small bulk to remove the greater portion of the hydrochloric acid. Add a solution of caustic potash to precipitate the iron, while the aluminum-potassium compound that forms is soluble.

Filter the iron with the pump, wash well with hot water, and discard the precipitate.*

To the filtrate add hydrochloric acid to slight acidity, and precipitate the alumina with freshly prepared ammonium sulphide. Wash with hot water. The heated precipitate is Al_2O_3. This subtracted from the weight of iron and alumina obtained in the foregoing gives the remainder of the iron.

4. To determine the calcium oxide.

The filtrate from **3** is treated with ammonium oxalate and determined as usual.

5. To determine the magnesium oxide.

Concentrate the filtrate from **4** to smaller bulk and proceed as before.

To determine the water.

Proceed as in fahlerz. The use of lead oxide is not necessary here.

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* Iron in a solution containing caustic potash cannot be thoroughly washed, and hence in the present case the alumina must be determined. Another method of separating iron and alumina is given in connection with the analysis of dolomite.

XV. Granite.

The constituents vary, but the analysis of a type is here described. It was found to contain silica, molybdenum sulphide, calcium, magnesium, alumina, potassium, sodium, ferrous and ferric iron, titanic and phosphoric acids, and water.

Fifteen grams should be finely pulverized, and bolted through a fine cloth. The bolting is necessary, as otherwise coarser particles of silica might not be acted upon by sodium carbonate when fused with that substance.

A. To determine the acids.

1. CO_2. Determined in the usual way.

2. To determine the TiO_2.[*] Bettel's method.

Place a gram of the substance in a porcelain crucible and add two grams of acid potassium sulphate. Mix with a platinum wire and moisten with a few drops of sulphuric acid. Place high over a small flame and heat three hours with the crucible closed. The flame should be so regulated as to send off a steady stream of sulphur trioxide.

Cool the crucible, and place the substance in a beaker of water, and let it stand over night to dissolve. The double salt, potassium-titanium sulphate, which has formed, is soluble in water. Filter. Wash with cold water and set the filtrate aside.

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[*] $TiO_2 + 4KHSO_4 = K_2Ti(SO_4)_3 + K_2SO_4$

Boiling: $K_2Ti(SO_4)_3 + 4H_2O = Ti(OH)_4 + 2KHSO_4 + H_2SO_4$.

Dry the precipitate, heat it in a porcelain crucible, and treat again with acid potassium sulphate and sulphuric acid to remove all titanium.

Unite the two filtrates in a six-litre flask and add four litres of water. Boil three hours, adding every fifteen minutes sulphurous acid, to reduce ferric iron, which might interfere with the precipitation of TiO_2. Boiling the potassium-titanium sulphate with much water precipitates titanic acid (H_4TiO_4). During the process the loss of water by evaporation should be supplied. Let stand over night and filter, bringing the liquid upon the paper by a siphon. Wash the precipitate with cold water. If the precipitate looks a little brown from iron oxide, dissolve the iron by pouring on a little sulphuric acid. Dry and ignite the precipitate as usual.

3. To determine the phosphoric acid.

Place a portion of the substance in a porcelain dish on the water-bath, add about 30^{cc} of nitric acid, and evaporate to dryness. This sets free the phosphoric acid. Add more water and nitric acid and filter with the pump. The residue on the filter is discarded.

Heat the filtrate to boiling, and to the hot solution add ammonium molybdate. This precipitates the phosphoric acid as ammonium phosphomolybdate. Set aside for twelve hours, on the addition of a little nitric acid, to insure complete precipitation. Filter with the pump and wash with ammonium nitrate (this is made by adding so much nitric acid to ammonia that it still reacts acid). It dissolves substances which may have been precipitated with the phosphate.

Dissolve the contents of the filter by pouring warm ammonia upon it. Precipitate the solution with magnesium ammonium chloride and determine as in previous cases.

The filtrate from the ammonium phosphomolybdate often contains more phosphoric acid; and heating and allowing it to stand with an excess of the ammonium molybdate will often give a second precipitate. This should receive the same treatment as the first portion.

4. To determine the silica.

Place in a platinum crucible two grams of sodium carbonate, a gram of the substance, and five grams of sodium carbonate. Mix all thoroughly with a platinum corkscrew. Heat for fifteen minutes with the crucible covered, over a Bunsen flame, to allow some of the carbon dioxide to escape. Then transfer to a blast lamp and heat, covered, to complete fusion, or until no more gas escapes. Blow air against the walls of the crucible, more easily to remove the contents. Remove the fused mass to a beaker, add water to the crucible, and heat to boiling. Repeat a number of times. Finally add dilute hydrochloric acid to dissolve all the substance adhering to the crucible.

Treat the contents of the beaker with dilute hydrochloric acid, as long as there is an evolution of gas, to decompose the carbonates. Heat to boiling until all the carbon dioxide is driven off.

Transfer the contents of the beaker to a porcelain dish and evaporate to dryness. Commence to stir with a glass rod as soon as crystals of common salt appear, as they tend to enclose other substances which would be estimated as silica.

When perfectly dry and fine add sufficient dilute hydrochloric acid to moisten well the powder. Leave for fifteen minutes on the water-bath to change the oxychlorides into normal chlorides.

Filter off the H_2SiO_3 with the pump and wash with hot water. Dry and place the substance with the filter folded over it, to enclose it, in a clean weighed platinum crucible. Press it down with the finger to make it fit snugly in the corner. Wipe the funnel with another small filter paper, and place it over the one enclosing the silica and moisten with a few drops of water.

Place the crucible on a triangle in a slanting position, and commence heating the outer edge with a very small flame, gradually increasing it and moving downwards. When the moisture is removed, employ the full flame until all is white. The substance is very fine and easily escapes, but the filter papers serve as covers to prevent loss. Such carefulness is necessary only with silicates, as other minerals contain the silica in layers and not in combination. When all is white, place the crucible in an upright position and heat ten minutes longer. Then transfer to a blast lamp and heat closed for ten minutes, to remove all moisture. Heat to constant weight.

Place some commercial hydrofluoric acid * in a platinum still, moisten the silica in the crucible with dilute sulphuric acid, and distill hydrofluoric acid into the crucible until it is three-fourths full. Place the crucible on the water-bath to remove the volatile SiF_4 which has formed. Remove the sulphuric acid with the direct flame. Cool and weigh. Repeat the distillation of hydrofluoric acid, etc., until constant weight is gained. The loss in weight represents the SiO_2.

B. To determine the bases.

1. Molybdenum.

The residue in the crucible is now treated with dilute hydrochloric acid and heated until all is dissolved. Add this to the filtrate from the silica and pass through it when cold a stream of sulphuretted hydrogen for half an hour. This precipitates MoS_3 and PtS_2, the latter having been dissolved from the platinum apparatus. This filtrate, **C**, heat at once to boiling to expel the sulphuretted hydrogen.

Pour yellow ammonium sulphide on the well-washed precipitate. This dissolves the MoS_3 and PtS_2 as double salts and leaves PbS and CuS on the filter, which may be estimated if in sufficient quantity.

Place the filtrate from the preceding in a porcelain crucible and evaporate to dryness. When dry, pass a current of burning hydrogen into the crucible, which is heated with a Bunsen flame. This reduces the

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* Pure hydrofluoric acid may now be purchased of the usual dealers.

MoS_3 to MoS_2 and the PtS_2 to Pt. After removing the flame introduce the stream of hydrogen until the crucible is cool. Weigh, and treat the substance with fuming nitric acid, which volatilizes the molybdenum and leaves the platinum.

2. To determine the alumina.

Heat the filtrate from 1 to boiling and oxidize with fuming nitric acid. Add a little ammonium chloride and precipitate with a small excess of ammonia. This precipitates the iron and aluminum. Filter. Acidulate the filtrate **D** and set it aside.

The precipitate is dried and placed with the filter ashes in a porcelain crucible and heated. It is then treated with hydrochloric acid on the water-bath until all is dissolved, save a small portion of H_2SiO_3, which passed through the filter in the beginning as H_4SiO_4. Filter the silica and add the amount to the first portion received.

Evaporate the filtrate from the silica almost to dryness to remove the excess of acid. Add about three grams of solid caustic soda, and leave five minutes on the water-bath, stirring with a platinum spatula. This precipitates all the substances except alumina. Filter, and set aside the precipitate.

Place the filtrate containing the alumina on the water-bath for a few minutes and acidify with hydrochloric acid. Precipitate with freshly prepared ammonium sulphide and determine as in phosphorite.

3. To determine the iron.

The precipitate that was set aside in **2** is dissolved in warm dilute hydrochloric acid. Ammonia is added to alkalinity, which precipitates the total amount of iron and titanium. After transferring the precipitate and the filter ash to a porcelain crucible, determine the weight. From the percentage obtained deduct the percentage of titanium previously obtained, to find the percentage of iron.

4. Manganese.

Granites frequently contain a small quantity of manganese, but if after fusion with sodium carbonate the substance is white or nearly so, manganese is absent, or is present in such small quantities that it cannot be weighed. If present, determine as in previous cases.

5. To determine the calcium.

The filtrate from **3** is added to filtrate **D**. Evaporate to small volume and treat as usual.

6. To determine the magnesium.

Proceed as in previous cases.

7. To determine the alkalis.

(*a*) K_2O.

Place a gram of the substance in a platinum crucible and moisten with sulphuric acid. Distill hydrofluoric acid into the crucible until nearly full. The hydrofluoric acid forms with silica H_2SiF_6, which the sulphuric acid decomposes into $SiF_4 + 2HF$, both of which are volatile.

After evaporating almost to dryness, distill more hydrofluoric acid into the crucible, and again evaporate on the water-bath to remove the silica. Then with the crucible closed, heat with the Bunsen flame to remove all the sulphuric acid.

Place the crucible on the water-bath, nearly fill with dilute hydrochloric acid, and decant into a large beaker. Continue until 200^{cc} of the acid has been used, completely to dissolve the sulphates. Boil the contents of the beaker fifteen minutes. If a gritty residue can be felt on the bottom of the beaker with a glass rod, it is silica. Filter, and repeat the treatment with sulphuric, hydrofluoric, and hydrochloric acids.

Precipitate the sulphuric acid of the sulphates with barium chloride, and without filtering, evaporate to dryness. When dry, add ammonia and acid ammonium carbonate. This precipitates all the substances except the potassium and sodium salts. Filter, wash, and reject the precipitate.

The filtrate containing potassium and sodium, as well as a little calcium and magnesium, is placed in a small platinum dish and evaporated to dryness on the water-bath, and heated with the direct flame to remove the ammonium salts. When cool add a little water and filter. The calcium and magnesium salts are difficult to remove. Add ammonium carbonate to the filtrate. Evaporate to dryness, heat to dull redness, treat with water and filter, as long as a precipitate continues to form on the addition of the carbonate. Ten or fifteen different treatments may be necessary. In evaporating the solution containing ammonium carbonate, the dish must be covered with a watch-glass during the evolution of gas, as the carbonate decomposes at 55°–60° and the escape of the gases might occasion loss. Upon the addition of the last portion of ammonium carbonate, let stand over night and filter next morning. Still a small quantity of magnesium will be in combination with the alkalis which cannot be separated by this method, but must be removed later.

The last filtrate is evaporated to dryness in a platinum dish and heated, covered, with a direct flame. Cool and weigh. Add a drop of hydrochloric acid and heat. Cool and weigh again. Continue to constant weight, which indicates the absence of ammonium salts. The hydrochloric acid keeps the magnesium as chloride, which might otherwise change into oxide. Each heating must be sufficient to melt the alkalis.

Dissolve the residue in a little water, and if it is not clear, filter. To the clear solution on the water-bath add about twenty drops of platinic chloride, and evaporate to dryness,* when the precipitate should be of a reddish color. If yellowish, all the Na_2PtCl_6 is not in solution. Add a few drops of water and tip the dish back and forth until the mass flows quietly. Na_2PtCl_6 crystallizes with two molecules of water, but it dissolves on adding a few more drops of water, and the mass is movable. Too much water would dissolve some K_2PtCl_6.

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* Do not allow the water-bath to boil, but evaporate, using as little heat as possible.

Filter the solution into a small flask. The filtrate should be deep red, otherwise not all the potassium is precipitated and more platinic chloride must be added. Rinse the dish containing the alkalis with equal parts of alcohol and water, and wash the precipitate five or six times with a volume of water and a half volume of alcohol. Now wash six times with a mixture of alcohol and ether. This produces a turbidity in the filtrate on account of $MgCl_2$, $PtCl_4$ (the exact formula is not known), which is insoluble in ether.

Dry the precipitate, place it over a weighed platinum crucible, and pour hot water on the K_2PtCl_6 to dissolve it. A small black residue will be found on the paper, which does not dissolve. This is platinous chloride, which was reduced from the platinic chloride, and may be discarded. Evaporate the solution to dryness on the water-bath, and heat in a thermostat at 105° to constant weight. From the amount of K_2PtCl_6, the K_2O can be determined.

(*b*) To determine the Na_2O.

The Na_2PtCl_6 contained in the flask with ether and alcohol is evaporated on the water-bath until the ether and a portion of the alcohol are volatilized. Place in the flask a two-holed rubber stopper, into which two glass tubes bent at right-angles project. To one tube connect the delivery tube of a hydrogen generator and pass sufficient hydrogen through the flask to displace the air. Shake the liquid that it may come in contact with the hydrogen, which reduces the

Na_2PtCl_6 to NaCl, HCl, and Pt. The hydrogen must go through for several hours until the solution is colorless.

When the reduction is complete, filter into a weighed platinum crucible and evaporate to dryness. Heat to redness, cool, and weigh. After adding a drop of hydrochloric acid, heat and weigh again. Repeat to constant weight. This gives the quantity of sodium chloride, together with a small amount of magnesium chloride.

Dissolve the substance in water and precipitate the magnesium with disodium phosphate and ammonia. From the amount of pyrophosphate obtained, compute the percentage of magnesium chloride. The data are thus at hand for determining the percentage of Na_2O.

8. To determine the ferrous oxide (FeO).* The Mitscherlich method.

A gram of the substance is placed in a dry, clean tube of hard glass about 40^{cm} long. Through a long funnel tube, introduce 10^{cc} of a solution of sodium carbonate. Add a drop of sulphuric acid, and when the action ceases, add another drop, and continue until 20^{cc} have been added. The carbon dioxide which is liberated displaces the air and prevents oxidation.

Melt the tube in the blast lamp to close it. Shake well, and heat for three hours in the Carius furnace at 260°–280°. Cool the tube and open it with a file scratch and small gas flame. Wash the contents into a beaker, dilute with water to a volume of half a litre, and titrate with a standard solution of potassium permanganate.

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* This determination can well be postponed until the student has had practice in titrating with potassium permanganate.

9. To determine the water.

Proceed as in phosphorite.

To prepare the chemically pure platinic chloride for alkali separations.

Clean six grams of platinum on the water-bath with dilute hydrochloric acid. Then add *aqua regia* and continue the additions until all the platinum is dissolved. Evaporate nearly to dryness, add a little water, and continue the evaporation, adding ten or fifteen successive portions of water until no further odor of nitrogen peroxide is apparent.

Filter the residue, heat the filtrate to boiling, add caustic soda to strong alkalinity, and a few drops of alcohol. Acidify with hydrochloric acid and add a solution of potassium chloride. Let stand over night and filter in the morning. Wash the precipitate with a dilute solution of potassium chloride.

Thoroughly dry the precipitate, transfer it to an evaporating dish, and crush to a fine powder. Remove it to a combustion tube about 40^{cm} in length. Place it in the combustion furnace and heat for half an hour with small flames while a stream of hydrogen passes through to reduce it to metallic platinum.

When cool transfer to an evaporating dish and wash several hundred times (1000–1200) with hot water, until a few drops of the washings give no precipitate with silver nitrate. When thoroughly washed transfer to an evaporating dish and dissolve in *aqua regia.* Continue evaporating and adding water until no odor of nitrogen peroxide is perceived. Dissolve the residue in water, making a dilute solution.

Remarks.

1. Ferrous iron.

If the specimen contains sulphides, by the Mitscherlich method described in the text, these have a tendency to reduce the ferric compounds to ferrous compounds, thereby giving too high a result in ferrous iron. This defect is remedied by a method devised by J. P. Cooke. The rock powder is decomposed on the water-bath, in an atmosphere of carbon dioxide, with sulphuric and hydrofluoric acids. A water-bath eight inches in diameter has perforations in its smallest rings. The outer ring contains a groove, which can hold a little water to make an air-tight joint with a glass funnel. There are two tubes on the sides of the bath, through one of which a stream of carbon dioxide flows from a generator. (Fig. 4.)

A gram of the rock powder is weighed into a platinum crucible of 40^{cc}–50^{cc} capacity, and 10^{cc} of dilute sulphuric acid are slowly added. The crucible is placed on the water-bath, which is heated to boiling. A glass funnel with the stem cut off is placed in the

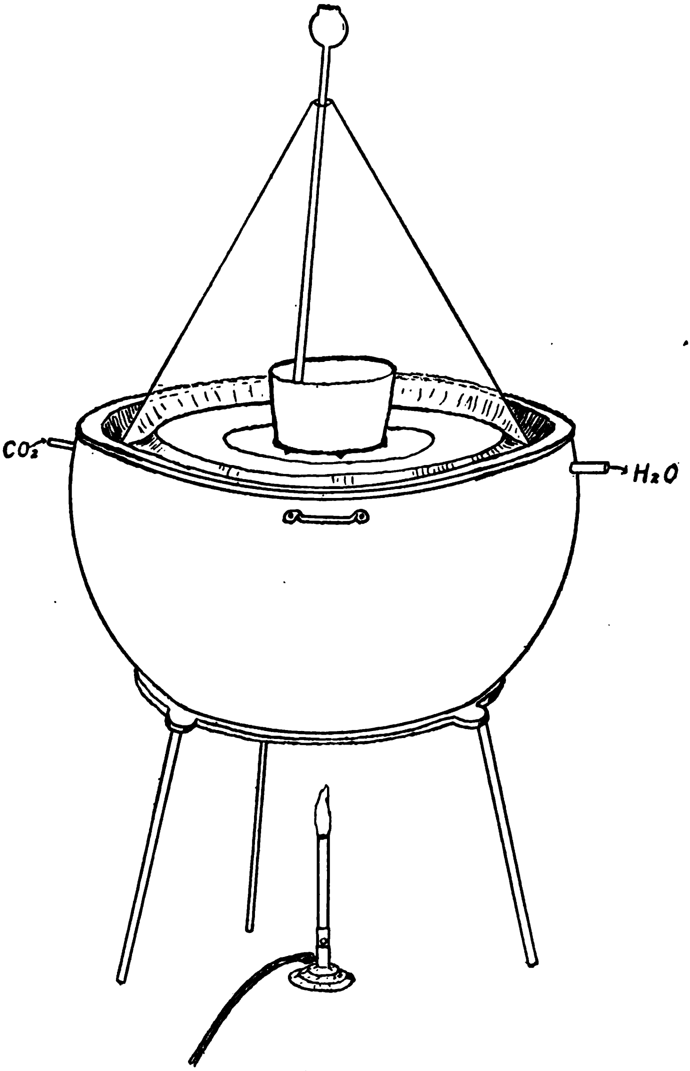

Fig. 4.

groove, and the stream of carbon dioxide is introduced. By means of a platinum funnel with a long stem for a stirrer, 10^{cc}–20^{cc} of hydrofluoric acid are added. The bath is kept boiling for half an hour, when it is allowed to cool, the stream of carbon dioxide continuing. The contents of the beaker are washed into a platinum dish and titrated with a standard solution of potassium permanganate.

2. The J. Lawrence Smith method of estimating the alkalis.

A half gram of the material is sufficient for this determination. The fine powder is mixed in a platinum crucible with the same weight of ammonium chloride and eight times as much alkali-free calcium carbonate. The crucible is then heated to bright redness for an hour. The cold crucible and its contents are placed in water in a porcelain evaporating dish, and boiled for some time, after crushing to a fine powder. This dissolves the alkalis with some calcium hydrate. It is filtered, the precipitate is discarded, and solutions of ammonium carbonate, ammonia, and a few drops of ammonium oxalate are added. Allow the substance to stand a few hours, filter into a platinum dish, evaporate to dryness, and heat the residue sufficiently to remove the ammonium salts.

Dissolve the residue in a little water. If the rock contains sulphides, add a few drops of a solution of barium chloride to precipitate the sulphates. A little ammonium carbonate solution is next added to precipitate the barium, and the trace of lime which may be present. If there are no sulphates, a few drops of a solution of ammonium oxalate are added, which precipitates lime more completely than ammonium carbonate. Filter, and to the filtrate add a few drops of hydrochloric acid and evaporate to dryness in a weighed platinum dish. This gives the potassium and sodium chlorides. The potassium chloride can be separated from the mixture as described on pages 80-81, and the sodium chloride can be determined by difference.

It may be well to make a blank test with the ammonium chloride and calcium carbonate for alkalis, and to apply any necessary correction.

3. To prepare the ammonium molybdate solution, used to precipitate phosphoric acid.

Dissolve 75 grams of ammonium molybdate in 500^{cc} distilled water, with the addition of a little ammonia, if necessary. If the solution is not clear it should be filtered and then poured, with constant stirring, into a mixture of 250^{cc} of concentrated nitric acid (Sp. G 1.40) and 250^{cc} distilled water. The freshly made molybdate solution must be allowed to stand in a warm place for several days. The clear solution is decanted or filtered for use. The solution will keep only a few months, as the molybdic acid is slowly precipitated. This is an expensive reagent and should not be wasted.

PART III

VOLUMETRIC ANALYSIS

PART III.

VOLUMETRIC ANALYSIS.

VOLUMETRIC analysis consists in adding from a burette a solution of known strength, called the standard solution, to a known quantity of substance in solution, until a definite reaction, as shown by an indicator, takes place. From the amount of the standard solution added, the percentage sought can be determined.

Indicators.

The chief substances used as indicators are litmus solution, which turns blue in contact with alkalis and red with acids; phenolphthaleïn solution, which is colorless in acid solutions and red in alkaline solutions; methyl orange solution, which is reddened by acids, and made yellow by alkalis; and neutral potassium chromate solution, the indicator used in titrating the halogens with silver nitrate; and starch solution, The solution of phenolphthaleïn is made by dissolving two grams of the crystals in 150^{cc} 95 per cent alcohol. The theory of indicators is discussed in some of the larger manuals.

General Remarks and Suggestions.

If only one determination is to be made, the gravimetric method would doubtless be chosen. If a number of similar determinations are required, the volumetric method is more expeditious, especially when the standard solution has been made and its value determined.

The burette, so important in volumetric analysis, consists of a straight tube of uniform bore, graduated into centimetres and tenths. By a little practice, the hundredths can be estimated with sufficient accuracy.

The Geissler form of burette is probably the most convenient. In this the solution is delivered through a glass stopcock. The stopcock should occasionally be rubbed with a little vaseline to secure easy action and close fitting.

The burette should be cleaned with fuming nitric acid, or pulverized potassium bichromate and sulphuric acid. Frequent cleanings are necessary when titrating with potassium permanganate.

Rinse two or three times with the standard solution before beginning the titration. In reading, hold the burette loosely between the thumb and forefinger, that it may assume a vertical direction. With the eyes on a level with the upper surface of the liquid, to avoid parallax, read each time from the top of the meniscus. It is not necessary to use a float.*

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* Zeitschr. angew. Chemie xv. 4.

After filling the burette, wait a short time before reading to allow any drops on the side to settle. Observe the same precaution after withdrawing any portion of the solution. In the beginning, see that the part of the burette below the stopcock is entirely filled. Keep the burette corked when standing with the standard solution.

Before beginning the titration, fill the burette to about the same height each time. On account of a possible variation in the bore, the observance of this precaution will insure greater accuracy.

As the bore of the tube is rarely uniform throughout, to secure the most accurate results it must be calibrated. The unit of volume is the " Mohr litre." This is the volume of 1000 grams of water at 17.5° C., which is near the temperature of the laboratory, and therefore a much more convenient unit than 4° C.

Fill the burette to the zero mark, with water. Then withdraw 5^{cc} each time into a small flask and weigh. Continue until all the liquid has been withdrawn. Keep a careful record of the results. Suppose, as has happened, that 5^{cc} between the 15^{cm} and 20^{cm} mark weigh 4.95 grams, and between the 25^{cm} and 30^{cm} mark 5.1 grams. In practice allowance can easily be made for these and similar discrepancies. It is not necessary to remove *exactly* five centimetres each time in calibrating. The amount can vary within a tenth of a centimetre. The temperature of the volumetric laboratory should obviously be kept as uniform as possible.

To secure accurate results in volumetric analysis, even greater carefulness is demanded than by the gravimetric process. The weights of the substances employed for the standard solutions must be determined with the greatest possible accuracy.

I. Titration with potassium permanganate.

This reagent oxidizes the substances. Other oxidizing agents similarly employed are potassium bichromate, potassium ferricyanide, iodine, and ferric chloride.

To prepare the solution.

Weigh 5 grams commercial potassium permanganate on the rough balance. Dissolve in hot water and dilute to a litre. Keep the solution in a dark place, and each time after using withdraw into the main portion any residue in the burette.*

If chemically pure potassium permanganate were always at hand, the value of a centimetre of the solution could be determined by a simple mathematical calculation. It is well, however, to become accustomed to working with impure materials.

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* Professor H. N. Morse and students of Johns Hopkins University have investigated the cause of the deterioration of permanganate solutions. They conclude that it deteriorates on account of the formation of manganese dioxide in the solution. If carefully filtered through asbestus or glass wool, it does not deteriorate in the dark or in diffused daylight. The case is different in direct sunlight. The solution once placed in the burette should be filtered before returning to the main portion. Careful attention to these details dispenses with the frequent determination of the strength of the solution. (See The American Chemical Journal xviii. 401.)

The two main reactions with permanganate titrations are:

A. $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

B. $5FeCl_2 + KMnO_4 + 8HCl = 5FeCl_3 + KCl + MnCl_2 + 4H_2O$.

Accurately weigh six or eight pieces of the purest piano wire,* .12–.15 of a gram in each. Wrap each portion with a piece of paper, on which its weight is written. Place them in a desiccator until needed. The wire should contain 99.7% of iron, but the amount can be gravimetrically determined.

Two portions of wire at a time are dissolved in four-ounce flasks having a bulb tube, valve, and plug similar to that used in determining the ferric oxide in siderite on page 39. Dissolve the iron in dilute sulphuric acid, hastening the action by gentle heat. The flask should be inclined at an angle of 45°. When all is dissolved, heat for a moment to boiling to expel the hydrogen, which has power to reduce permanganate solution. Cool and wash the contents of the flask into a litre beaker. Add 50^{cc} of dilute sulphuric acid and dilute each time with water to $\frac{1}{2}$ of a litre. The water used in these determinations should be freshly boiled to expel oxygen. Place the beaker on a piece of white paper and add permanganate solution from the burette until a light pink color remains a moment or two in the liquid. The permanganate thus serves as an indicator, and no other is necessary.

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* Remove any oxide on the wire by rubbing it with sandpaper.

In this way ascertain the amount of iron that corresponds to a cubic centimetre of the solution, and continue until two consecutive results agree to the fifth decimal place.

An illustration:

(1) 1^{cc} of the solution corresponded to .01010Fe
(2) 1^{cc} “ “ “ “ “ .00881 “
(3) 1^{cc} “ “ “ “ “ .00805 “
(4) 1^{cc} “ “ “ “ “ .00785 “
(5) 1^{cc} “ “ “ “ “ .00798 “
(6) 1^{cc} “ “ “ “ “ .00800 “
(7) 1^{cc} “ “ “ “ “ .00802 “
(8) 1^{cc} “ “ “ “ “ .00802 “

When the value of the solution is determined the rest follows easily.

1. To determine the percentage of iron in siderite, $FeCO_3$.

Two different tests are made in all these determinations.

A half gram of the finely pulverized substance is placed in each of the two flasks, dissolved in dilute hydrochloric acid, and treated in every respect like the piano wire. Cool, wash into a beaker glass, and add 10^{cc} of a solution of manganese sulphate to counteract the reducing power of hydrochloric acid. Manganese sulphate is necessary whenever hydrochloric acid is used as the solvent. Ores of iron are more easily soluble in hydrochloric than in sulphuric acid. Multiply the number of centimetres of the solution required by the value of a centimetre and divide by the weight of siderite used, to obtain the percentage of iron.

An analysis resulted:

(*a*) 46.27% FeO
(*b*) 46.33% "

A gravimetric analysis of the same specimen gave 46.34% FeO.

2. To determine the percentage of iron in ferrous sulphate, $FeSO_4, 7H_2O$.

Weigh out a portion of the substance, about 0.5 gram in each beaker glass used for the titrations. Dissolve the salt in 200^{cc} water, add 50^{cc} dilute sulphuric acid, and titrate as usual.

3. To determine the percentage of iron in limonite, $2Fe_2O_3, 3H_2O$.

A half gram of the powdered mineral is placed in each of the two flasks, and boiled with dilute hydrochloric acid until the silica is white on the bottom. Then reduce the iron with a small quantity of chemically pure zinc, all of which must be dissolved. Boil to expel the hydrogen. Cool, wash into a beaker glass, and determine as usual.

An analysis resulted:

(*a*) 47.08% Fe_2O_3
(*b*) 47.15% "

4. Haematite, Fe_2O_3.

Proceed as in limonite.

5. Magnetite.

Composition: FeO, Fe_2O_3.

(*a*) To determine FeO.

Place a half gram of the pulverized substance in each of the flasks, and dissolve it in dilute hydrochloric acid. Heat to boiling until the silica is white. Cool, and transfer to a beaker with 10^{cc} of manganese sulphate solution, and titrate.

An analysis showed:

29.03% FeO
29.28% "

(*b*) To determine the total amount of iron.

Treat as in (*a*). When all is dissolved, reduce the iron with pure zinc, and titrate as usual.

Knowing the amount of FeO and the total amount of iron, the percentage of Fe_2O_3 can be determined.

An analysis showed:

62.51% Fe_2O_3
62.57% "

6. To determine the purity of black oxide of manganese (MnO_2).

Dissolve .4–.5 gram of piano wire in the flask with dilute hydrochloric acid, and remove the hydrogen by boiling. Cut $1\frac{1}{2}^{cm}$ from the bottom of a test-tube, and 2^{cm} from an ordinary glass tube closed at one end. A piece of platinum wire is wound around the portion of test-tube, while an end of the wire is made into a loop for suspending on the balance. The glass tube is placed in the test-tube. Weigh into the inner tube .2 gram of the manganese dioxide. Place this tube and its contents in the iron solution, and heat until the silica that may be contained in the manganese has become white. Then wash the contents of the flask into the beaker, add the manganese sulphate solution, and titrate as usual.

Make the computation as follows: Multiply the number of centimetres of the permanganate solution used by its value. Subtract the product from the amount of piano wire taken. The difference is the quantity of iron oxidized by the manganese dioxide employed.

2Fe is oxidized by MnO_2; or in the ratio of 112 to 87. Multiply the foregoing difference by $\frac{87}{112}$ and divide the product by the weight of the manganese dioxide used, to find the percentage required.

Two analyses resulted:

(*a*) 66.88% MnO_2
(*b*) 66.88% "

7. KNO_3.

To determine its purity.

Place in a half-litre flask a gram of piano wire. The flask is fitted with a two-holed rubber stopper, into which project glass tubes, bent at right angles. One tube is closed with a piece of rubber tubing and glass plug; the same is on the end of the second tube, the rubber connection containing a slit for the escape of gases.

Dissolve the iron in dilute sulphuric acid and heat to drive off the hydrogen. Cool in a dish of water, with a stream of carbon dioxide passing through the flask. Then quickly introduce into the flask .2 gram of potassium nitrate weighed as the manganese dioxide in **4.** Boil the contents of the flask ten or fifteen minutes, while a stream of carbon dioxide passes through. Continue until the dark green color disappears and a lighter yellowish-green results.

Cool in a vessel of water as at first. Pour the contents of the flask into a beaker and titrate as usual.

Compute as in the case of manganese dioxide, remembering that 3Fe is oxidized by KNO_3.

Analysis resulted:

(*a*) 93.55% KNO_3
(*b*) 93.54% "

Remarks.

1. The method of standardizing the potassium permanganate solution with iron wire is known as Marguerite's method. Ferrous ammonium sulphate and oxalic acid are used for the same purpose.

2. There are objections to the use of zinc for the reduction of ferric compounds. It often contains iron, and it reduces titanium compounds, which are again oxidized by the permanganate. The process also introduces another metal into the solution. To obviate these difficulties, the ferric compounds are often reduced with hydrogen sulphide, while the acid solution of the iron is gently warmed in the flask. Reduction is complete when a drop of the iron solution is not colored red by a solution of potassium sulphocyanate. The operation usually requires about thirty minutes. The excess of hydrogen sulphide is removed by introducing a stream of carbon dioxide, while the flask is kept warm by a small flame. Lead paper is used to indicate the disappearance of the hydrogen sulphide.

Reactions:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$
$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S.$$

3. The reason for adding the manganese sulphate solution.

The effect of the manganous salt is due to the reaction with the permanganate, and the formation of tervalent or tetravalent manganese compounds, which react on the ferrous salt, these successive reactions occurring more rapidly than that of the permanganate on hydrochloric acid. (Baxter and Fremont in the Am. Chem. J.)

II. Titration with potassium bichromate.

The molecular weight of potassium bichromate is 294, and in acid solution it yields 48 parts by weight of available oxygen, as follows: $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$.

As eight grams of oxygen are equivalent to one gram of hydrogen, a normal solution of potassium bichromate will contain eight grams of available oxygen. This would require one-sixth of the molecular weight, or 49 grams per litre.

Weigh six or seven grams of the pulverized bichromate on the rough balance, and dry as described in the analysis of potassium bichromate, page 22. To prepare a deci-normal solution, weigh out exactly 4.9 grams of the dried salt and add sufficient water to make a litre of the solution. If a pure salt is used, which is quite easily obtained, it is not necessary to standardize the solution. The oxidation of ferrous iron to ferric iron by potassium bichromate is shown by the following equations:

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O$$

It is thus shown that 294 grams of bichromate oxidizes 336 grams of ferrous to ferric iron, and 4.9 grams of the salt would oxidize 5.6 grams of iron.

A cubic centimetre of the solution would therefore oxidize 0.0056 gram of iron.

To find the percentage of iron in any given specimen.

Multiply the number of centimetres required in any given analysis by 0.0056, and divide the product by the weight of the ore taken.

It is not necessary to use manganese sulphate in the titrations with potassium bichromate.

To find the end of the reaction.

Place twenty or thirty small drops of distilled water upon a white-glazed porcelain tile, and touch each drop with a crystal of potassium ferricyanide. (The crystal must be free from potassium ferrocyanide,) The ferricyanide gives a blue color with ferrous salts, but not with ferric salts. The bichromate solution is carefully added from the burette until the blue color exactly disappears. The same substances that were determined with the permanganate solution can now be determined with the bichromate solution and in the same order. Write the equations that express the reactions in each analysis.

III. Titration with silver nitrate. Exercises in the preparation of normal solutions.

To prepare a one-tenth normal solution, a decinormal solution, of silver nitrate.*

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* A normal solution of silver nitrate contains 170 grams of the salt dissolved in a litre of water (notice that 170 is the molecular weight).

A normal solution as defined by Mohr contains in one litre

Pulverize 18 grams of silver nitrate, and dry it in the air-bath at 110° to constant weight. Weigh out 17 grams of the dry powder and dissolve in a litre of water.

Place about two grams chemically pure sodium chloride * in a porcelain crucible, heat to melting with a blast lamp, if necessary, to remove all moisture. Let cool in a desiccator, crush into small pieces, and transfer to a weighing tube.

Weigh out .10–.15 gram of the salt in a 200^{cc} glass bottle, with a closely fitting ground stopper. Dissolve the salt in 80^{cc} of water and add a cubic centimetre of nitric acid, which assists in collecting

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one equivalent of the active reagent in grams. The "equivalent in grams" has been defined as "that quantity of the active reagent which contains, replaces, unites with, or in any way directly or indirectly brings into reaction one gram of hydrogen." A normal solution of hydrochloric acid would contain 36.45 grams of the gas to the litre; while one of sulphuric acid would contain 49 grams, half the molecular weight, as sulphuric acid contains two atoms of replaceable hydrogen.

* To prepare pure sodium chloride: Make a strong solution of the best commercial sodium chloride obtainable, and saturate with HCl gas, obtained by heating the strong commercial hydrochloric acid. The delivery tube should terminate in a glass funnel, the mouth of which should project into the salt solution, to prevent a clogging of the tube. The pure salt will be precipitated. The mother liquid should be drawn from the precipitate with a filter pump, the salt pressed between filter papers, and heated in an evaporating dish to remove hydrochloric acid.

the precipitate. Heat on the water-bath to 60°–70°, and add a few cubic centimetres of silver nitrate solution from the burette. With the stopper in the bottle, shake violently until the precipitate collects on the bottom and the liquid is clear. Continue cautiously to add the silver nitrate solution as long as a precipitate continues to form. When two consecutive results agree to the fourth decimal place, they may be taken as the value of the solution.

A one-tenth normal solution of silver nitrate contains .0170 gram of the salt in a cubic centimetre. Suppose a centimetre of the solution prepared shows a value of $.0173^{g}$. The addition of a certain amount of water is necessary.

The amount of water to be added is easily determined. Measure the portion of the solution that remains. Multiply the number of centimetres by .0003, the difference in value of a centimetre between the normal solution and the solution which has been made. The product is divided by .0170, and the quotient represents the additional water required.

If, on the other hand, the solution is too weak and shows a value of .0167 gram of the salt to the cubic centimetre, multiply the number of centimetres of the solution by .0003, which shows the amount of the silver nitrate to be added.

To determine the percentage of hydrocyanic acid in a solution. Liebig's method.

Measure 5^{cc} of the commercial HCN in the glass-stoppered bottle of 200^{cc} capacity, add water and a very small piece of sodium chloride. The salt serves as an indicator. Add silver nitrate to the warm solution until a precipitate forms. AgCN is soluble in HCN, and no precipitate of AgCl will appear until the HCN is exactly neutralized. The precipitate AgCl is more plainly seen than AgCN.

To prepare a normal solution of hydrochloric acid. This should contain 36.4 grams of the gas to a litre of water.

Into a bottle with a glass stopper, of 10^{cc} capacity, weigh a half gram of the dilute hydrochloric acid to be found on the laboratory shelves. Transfer the hydrochloric acid to the glass-stoppered bottle before used. Dilute to 100^{cc}, add nitric acid, and use the silver nitrate solution as in the common salt.

Suppose the acid is found to contain 20.42% of HCl gas, which would be 204.2 parts in 1000. Then $\frac{1000}{204.2} \times 36.4$ the mol.w. of $HCl = 178.3$. Take therefore 178.3 grams of the dilute acid and dilute with water to a litre. If this should not prove a normal solution, add water or the dilute acid as the case may require.

By the use of the one-tenth normal silver nitrate solution, make one-tenth normal solutions of potassium bromide and potassium iodide; also of sodium bromide and sodium iodide.

Alkalimetry.

In these determinations, litmus solution is used as an indicator. It is prepared as follows: Boil ten grams of powdered litmus in 100^{cc} of distilled water. Filter, and divide the filtrate into two portions. One part is weakly acidified with nitric acid and the two portions are mixed. Add two drops of the solution to 200^{cc} of water and test the sensitiveness with a drop of acid.

When litmus is used as an indicator in determining the alkaline carbonates, as the CO_2 acts upon the litmus, the liquid must be boiled to expel the gas. The alcoholic solution of phenolphthaleïn can be used in most determinations in alkalimetry and acidimetry. When used, boiling to expel the CO_2 is not necessary.

With the normal solution of hydrochloric acid determine the strength of the ammonia water on the laboratory shelves. Analyze also the various samples available of sodium carbonate and bicarbonate, potassium carbonate and bicarbonate, and lithium carbonate, and ammonium carbonate. Boil the solutions to expel the CO_2, which is liberated on the addition of hydrochloric acid.

To make a normal solution of caustic soda.

In the small glass bottle, weigh about .5 gram of the solution at hand. Dilute this in the large beaker with 200^{cc} of water, previously boiled to expel the CO_2 which distilled water sometimes contains. Using the litmus solution as an indicator, titrate with the normal hydrochloric acid. Having determined the strength of the caustic soda solution, the normal solution is made from it, as in the case of hydrochloric acid.

In the same manner, prepare a normal solution of caustic potash.

Acidimetry.

With the normal solution of caustic soda, determine the strength of the sulphuric, nitric, hydrochloric, and acetic acids that are used in the laboratory. Make normal solutions of all the acids, using both the normal solutions of caustic soda and caustic potash.

With the normal solution of sulphuric acid, using methyl orange as an indicator, which is not affected by CO_2, determine the purity of the various alkaline carbonates at hand. Compare the results with those obtained from the normal hydrochloric acid.

IV. Iodimetry.

To prepare the reagents.

(*a*) Iodine solution.

Weigh between two watch-glasses held together by a clamp 5 grams of commercial iodine. Add this to 12 grams of potassium iodide dissolved in 25^{cc} of water and dilute to a litre. Before use, it should be well shaken to form a homogeneous mixture.

(*b*) To make the dilute sulphurous acid solution.

The solution should contain no more than 4% of the acid, and the following reaction takes place:

$$2I + SO_2 + 2H_2O = 2HI + H_2SO_4$$

If it contains more than 4%, the H_2SO_4 reacts upon the HI, forming $2I + H_2O + SO_2$.

Place 12^{cc} of a saturated solution of SO_2 in a large flask and add 5 litres of water. Keep the solution in a cool place and shake well each time before using. A glass-stoppered bottle of 200^{cc}–250^{cc} capacity is used as a measure. This is filled, and the stopper set in carefully, that the bottle may contain no air bubbles. The outside is washed with distilled water.

(*c*) To prepare the starch solution which is used as an indicator.

Pulverize 2 grams of starch and add to it a few centimetres of cold water. Transfer this to a litre of water at 80°. Heat to boiling in a large porcelain evaporating dish, and boil vigorously for 10–15 minutes, using three burners, if necessary. Allow the sediment to settle and siphon the clear liquid into a bottle.

Test the starch by adding a few drops to 200^{cc} of water. A single drop of iodine solution should give a pronounced blue color.

(*d*) To prepare iodine.

Slowly sublime a good quality of the commercial article between two small porcelain evaporating dishes. Pulverize the sublimate and let it stand in a desiccator, over sulphuric acid. The desiccator should be free from fat.

To determine the value of the iodine solution (solution *a*).

Place in a large beaker one measure of the dilute H_2SO_3 solution. Rinse the bottle twice with water.* With the beaker standing on white paper, add a cubic centimetre of the starch solution, and the iodine solution from a burette until the blue color appears.

Secondly, place another measure of H_2SO_3 solution in the beakers, and add to it .15 gram of iodine from the desiccator. Titrate with the iodine solution until the blue color is seen. Subtract the amount of the iodine solution now required from the amount when only the H_2SO_3 was used. Divide the amount of iodine taken by the difference and the quotient is the value sought.

1. To determine the strength of a solution of sulphuretted hydrogen.

Take 25^{cc} of dilute H_2S water, add a few drops of the starch solution, and titrate with the iodine solution.

Reaction: $H_2S + 2I = 2HI + S$
$17 : 1\cdot27$

Multiply the number of centimetres of the iodine solution taken by the value, and the product by $\frac{17}{127}$, then by 4 to get the number of parts in 100, or the percentage of H_2S.

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* The distilled water used in connection with H_2SO_3 should be boiled to expel oxygen.

2. To determine the degree of purity of sodium thiosulphate, $Na_2S_2O_3, 5H_2O$.

Dissolve a gram of the substance in water, add the starch solution as usual, and titrate with the solution of iodine.

Reaction:

$$2Na_2S_2O_3,\ 5H_2O + 2I = 2NaI + Na_2S_4O_6$$

$$Na_2S_2O_3,\ 5H_2O : I :: 248 : 127$$

Multiply the number of centimetres of the iodine solution employed by $\frac{248}{127}$ and divide the product by the amount of sodium salt taken to find the percentage.

3. To determine the degree of purity of potassium iodide.

In the analysis, chlorine water is used (one part of a saturated solution of chlorine and one part water).

Reaction:

$$KI + 6Cl + 3H_2O = HIO_3 + KCl + 5HCl$$

The value of the chlorine water is determined at the beginning and end of the analysis, and the average of the two results is used. The following is the method:

25^{cc} of the chlorine water is placed in a large beaker glass. A measure of the H_2SO_3, some crystals of KI, and starch solution are added. Titrate with the solution of iodine.

About .2 gram of the potassium iodide is dissolved in water in a cylinder with a good glass stopper. A little carbon disulphide is added. From a burette, chlorine water is dropped into the cylinder until the violet color is removed.

The computation: Multiply the value of the iodine solution (*a*) by the quantity of the solution equivalent to 1^{cc} of the chlorine water. This gives the value of α (alpha), which is the iodine equivalent to 1^{cc} of the chlorine water.

Multiply the value of α by one-sixth of the number of centimetres of the chlorine water required for the quantity of potassium iodide used. Multiply the product by 1.30 and divide by the weight of potassium iodide taken to find the percentage required.

$KI : I :: 166 : 127 :: 1.30 : 1$

Two analyses resulted:

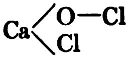
(*a*) 98.05% KI
(*b*) 98.02% "

4. To determine the purity of potassium bromide. A small portion of the substance is dissolved in a porcelain evaporating dish, heated to boiling, and kept at that temperature while chlorine water is dropped from a burette until the yellow color has disappeared. Find the value of α and compute as in the case of potassium iodide.

Two analyses resulted:

(*a*) 98.92% KBr
(*b*) 98.90% "

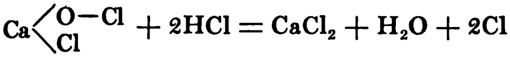
5. To determine the percentage of working chlorine in bleaching powder:



$$\mathrm{Ca}\begin{cases}\mathrm{O{-}Cl}\\ \mathrm{Cl}\end{cases}$$

Weigh ten grams of the substance, transfer to a mortar, add a little water, and digest. The powder would float on the surface if too much water were used. When all is wet pour into a measuring cylinder, and add water to make a volume of half a litre. This must be well shaken before using. 50^{cc} are used at a time, which therefore contains a gram of the substance.

Place the 50^{cc} in a beaker glass. Slightly acidify with hydrochloric acid. Add crystals of potassium iodide and enough measures of H_2SO_3 to make the solution colorless, using the starch, titrate with the iodine solution.



$$\mathrm{Ca}\begin{cases}\mathrm{O{-}Cl}\\ \mathrm{Cl}\end{cases} + 2HCl = CaCl_2 + H_2O + 2Cl$$

Two analyses resulted:

(*a*) 14.50% working chlorine
(*b*) 14.58% " "

6. To determine the percentage of purity of MnO_2. Bunsen's apparatus is used. This consists of a glass flask of 100^{cc} capacity, connected with a retort of a shape adapted to the purpose.

Weigh out .1–.2 gram of the manganese dioxide, place it in the flask, and add 50^{cc} dilute hydrochloric acid. The retort should contain about 100^{cc} of a ten per cent solution of potassium iodide. The flask and retort are connected and a stream of CO_2 introduced into the flask to drive out the air.* The flask is then heated, and about 25^{cc} is allowed to distill into the retort. The liberated chlorine sets free the iodine of the potassium iodide. The contents of the retort are poured into a beaker, allowed to cool, and one or two measures of H_2SO_3 are added, sufficient to make the liquid colorless. The liquid is then titrated with iodine solution, the starch being used as an indicator. From the amount of the iodine solution necessary the percentage can be computed as follows: Subtract the number of centimetres of iodine solution used from the iodine equivalent of the H_2SO_3 and multiply the difference by the value of a. The product obtained should be multiplied by $\frac{87}{254}$.

Reactions: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. $2KI + 2Cl = 2KCl + I_2$. MnO_2 is the equivalent of 2I. $MnO_2 : 2I :: 87 : 254$.

An analysis resulted:

(1) 72.81% MnO_2
(2) 72.75% "

7. To determine the purity of potassium bichromate, $K_2Cr_2O_7$.

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[*] The use of CO_2 is not absolutely essential in the determination.

The method and apparatus are precisely similar to what was used in **6**.

Reactions: $K_2Cr_2O_7 + 14HCl = 7H_2O + 6Cl + 2KCl + 2CrCl_3$.

$6Cl + 6KI = 6KCl + 6I$.

$K_2Cr_2O_7 : 6I :: 294 : 762$.

An analysis resulted:

(1) 99.95% $K_2Cr_2O_7$
(2) 99.90% "

PART IV

THE ANALYSIS OF ORDINARY DRINKING WATER

PART IV.

THE ANALYSIS OF ORDINARY DRINKING WATER.

To prepare the solutions.

(*a*) The lime-water.

Take 200 grams of freshly burned lime, add a little water, and when decomposed add water until it is about the consistency of cream. Let it settle, and decant the clear liquid into a large bottle. It should be filtered before using.

(*b*) The one-tenth normal solution of silver nitrate.

It can be made with sufficient accuracy for these analyses by dissolving 17 grams of the dry powder in a litre of water.

(*c*) The one-tenth normal barium chloride solution.

Dissolve 12.2 grams of the pure crystals ($BaCl_2$, $2H_2O$) in a litre of water.

(*d*) The neutral potassium chromate solution.

The commercial article should be entirely freed from chlorides by repeated crystallizations in water. Dissolve ten grams of the pure, air-dried salt in a litre of water.

(*e*) The solution of oxalic acid.

Dissolve 2.864 grams of pure oxalic acid crystals in a litre of water. Usually a cubic centimetre of this solution will exactly neutralize a like volume of the lime-water.

(*f*) The Nessler reagent.

Dissolve 17½ grams potassium iodide and 6½ grams of mercuric chloride in 400^{cc} of boiling water. When cool, add a cold saturated solution of mercuric chloride until a little of the red precipitate which forms (HgI_2) remains in the liquid. At first it is dissolved as rapidly as it forms. Then add 80 grams of solid caustic potash and dilute with sufficient water to make 500^{cc}.

(*g*) The permanganate solution.

Dissolve 200 grams of solid caustic potash and 8 grams of crystallized potassium permanganate in two litres of distilled water which is free from ammonia. Distill off one litre of water from the solution, testing the last portions of the distillate with the Nessler reagent to ascertain if all ammonia is removed. If not, add more water and continue the distillation. When the operation is finished there should be a litre of the solution.

(*h*) The stronger ammonium chloride solution.

Dissolve 3.15 grams of pure ammonium chloride in a litre of distilled water that is entirely free from ammonia. Prepare the water by repeated distillations, if necessary.

(*i*) The weaker ammonium chloride solution.

Take 5^{cc} of the stronger solution, to which add 495^{cc}

of pure distilled water. A centimetre of this solution will contain the hundredth of a milligram of ammonia.

(*j*) Sulphanilic acid.

Dissolve one gram of the acid in 100^{cc} of hot water.

(*k*) Naphthylamine hydrochloride.

A half gram of the salt is boiled for ten minutes in 100^{cc} distilled water. The volume must be kept constant by additions of water.

(*l*) The standard sodium nitrite solution.

To a solution of silver nitrate is added a cold solution of sodium nitrite as long as a precipitate continues to form. The precipitate of silver nitrite is filtered, washed in cold water, and then dissolved in boiling water. The solution is concentrated on the water-bath until crystals of silver nitrite are formed. These are filtered and dried in a dark place in a vacuum and kept in a black bottle.

Dissolve 0.22 gram of the dry silver nitrite in hot water. Decompose with a slight excess of sodium chloride, and dilute to one litre. When the precipitated silver chloride has settled, remove 5^{cc} of the clear liquid and add sufficient distilled water to make a litre. A cubic centimetre of this second solution, which is the standard solution, will contain an amount of nitrite equivalent to 0.0001 milligram of nitrogen. It should be kept in small bottles entirely filled with the solution to prevent the oxidation to nitrate.

(*m*) Standard sodium chloride solution.

Dissolve 1.6479 grams pure fused NaCl in one litre distilled water. Each cubic centimetre will contain one milligram of chlorine.

(*n*) Phenolsulphonic acid.

Place 370 grams of pure concentrated sulphuric acid in a flask with 30 grams of pure phenol, and keep for six hours in a bath of boiling water. The reaction:

$$C_6H_5OH + 2H_2SO_4 = C_6H_3OH(SO_3H)_2 + 2H_2O$$

(*o*) Standard potassium nitrate solution.

Dissolve 0.7221 gram of pure KNO_3 in one litre of distilled water. Evaporate 10^{cc} of this solution to dryness on the water-bath. Thoroughly moisten the residue with 2^{cc} of the phenolsulphonic acid and dilute to a litre. A cubic centimetre of this solution will correspond to 0.001 milligram nitrogen.

The analysis of water.

1. To determine the total amount of solid matter.

In a cleaned and weighed platinum dish of 150^{cc}–200^{cc} capacity, evaporate a litre of the water to dryness on the water-bath. Use pure water in the bath for this evaporation, in order that matter from the water may not collect on the outside of the dish. Heat the dry residue to constant weight at 130°.*

2. To determine the silica.

Moisten the residue in the platinum dish with a few drops of concentrated hydrochloric acid, and add 50^{cc} of water. Let it stand a short time and filter. Determine as usual.

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* In water analyses the quantity in 100,000 parts is usually estimated. Therefore as 1000 parts were taken in the beginning, multiply this and the following results by 100.

3. To determine the iron and alumina.*

The filtrate from 2 is oxidized with a few drops of fuming nitric acid, heated to boiling, and a small quantity of ammonium chloride is added, and ammonia to slight alkalinity. Boil to expel the excess of ammonia. Filter, and determine as usual.

4. To determine the CaO.

Proceed as in previous cases.

5. To determine the MgO.

Evaporate the filtrate from 4 to smaller bulk and precipitate with ammonium carbonate.

6. To determine the sodium, potassium, and lithium.

Evaporate the filtrate from 5 in a platinum dish to dryness on the water-bath and with a free flame remove the ammonium salts.

Dissolve the residue in a small quantity of water, and filter through a small paper into a weighed platinum crucible. Evaporate to dryness, heat to redness, cool, and weigh.

Having previously shown, with the spectroscope, the presence of lithium in the residue of an evaporated portion of the water, treat the substance in the crucible with a mixture of equal parts of anhydrous alcohol and ether. This dissolves the lithium chloride, but does not affect the potassium and sodium salts.

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* These are usually present in small quantities, and are estimated together. If, for any reason, it is desirable to separate them, it can be done, as in dolomite, phosphorite and granite, Part Second.

Evaporate the alcoholic extract to dryness on the water-bath, heat to redness, and weigh. If desirable to separate the potassium from the sodium, the method is the same as in the case of granite, Part Second.

To determine the sodium, potassium, and lithium. Second method.

Evaporate 500^{cc} of the water to dryness in a platinum or porcelain dish, add one-fourth of a gram of barium hydrate and a little distilled water to the dry residue, and heat to boiling. Filter and discard the precipitate. The filtrate contains the alkalis as chlorides and nitrates. The excess of barium is removed with a little ammonium carbonate solution. The precipitate is discarded, and the filtrate is evaporated to dryness in a porcelain or platinum dish. The residue is carefully ignited on the addition of a little solid ammonium chloride to change to alkali chlorides. A little warm water is added, and the substance is filtered through a small funnel into a weighed platinum or porcelain crucible. It is evaporated to dryness, and ignited on the addition of a little solid ammonium chloride.

When the alkalis are determined by this process, the magnesium can be precipitated in the usual way by sodium phosphate and ammonia, which is often the more satisfactory process.

7. To determine the chlorine.

Present as chlorides.

Bring 50^{cc} of the water into a beaker, add two or three drops of the neutral potassium chromate solution, which serves as an indicator. Titrate with the one-tenth normal solution of silver nitrate until a light red precipitate appears. The amount of nitrate taken multiplied by 7.1 gives the parts of chlorine in 100,000 parts of the water.

8. To determine the sulphates.

If the water is not entirely clear, filter 100^{cc} into a beaker glass, add 5^{cc}–10^{cc} of hydrochloric acid, and heat to boiling. Precipitate with a few drops of barium chloride solution.

9. To determine the carbon dioxide. Pettenkofer's method.

Free and loosely united.

Place 100^{cc} of the freshly drawn water in a flask, and add 45^{cc} of clear lime-water, 3^{cc} of a nearly saturated solution of calcium chloride, and 2^{cc} of a saturated solution of ammonium chloride, 150^{cc} in all. The flask is tightly corked, well shaken, and left for twelve hours.

Withdraw 10^{cc} of the clear liquid with a pipette, and place it in a small beaker. Add a few drops of litmus solution, and titrate with the solution of oxalic acid until a pink color results.

Determine, using the litmus solution, the amount of oxalic acid that neutralizes 45^{cc} of lime-water. Multiply the number of centimetres of oxalic acid required for the 10^{cc} of the flask by fifteen (as there were 150^{cc} in the flask), subtract the product from the amount of oxalic acid corresponding to the 45^{cc} of lime-water, and the difference is the quantity of CO_2 in 100,000 parts of the water.

10. To determine the free ammonia.

Place 500^{cc} of the freshly drawn * water in a litre flask connected with a Liebig condenser and distill off 200^{cc}. Before beginning the work, distill pure water through the apparatus for two hours to remove all the ammonia.

Place 50^{cc} of the distillate in one Nessler glass and the same quantity of pure distilled water in another. Add to each 2^{cc} of the Nessler reagent; and the dilute ammonium chloride solution to the glass containing the pure distilled water until it has the same color as the contents of the other glass. Multiply the number of centimetres required by four, and the product by two, to find the number of centimetres of the ammonium chloride solution that would be required for a litre of water. All the free ammonia in 500^{cc} of water will be contained in the 200^{cc} of the distillate.

Reaction:

$$2(2KI, HgI_2) + NH_3 + 3KOH = NH_2HgOHgI \\ + 7KI + 2H_2O$$

11. To determine the albuminoid ammonia.

To the 300^{cc} of water remaining in the litre flask add 50^{cc} of the permanganate solution, and again distill off 200^{cc}. This distillate contains all the albuminoid ammonia transformed by the permanganate solution into free ammonia. Nesslerize 50^{cc} as in 10.

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* It should be drawn not more than twenty-four hours at the longest before the determination is made.

According to Wanklyn the potability of water is determined by the quantity of albuminoid ammonia it contains. He says: " Albuminoid ammonia above .10 per million begins to be a very suspicious sign, and over .15 it ought to condemn a water absolutely. When the albuminoid ammonia amounts to .05, then the proportion of free ammonia becomes an element in the calculation; and I should be inclined to regard with some suspicion a water yielding a considerable quantity of free ammonia along with more than .05 parts of albuminoid ammonia per million." * Other authorities contend that a greater amount of the ammonias is permissible in a good water.

12. To determine the nitrates.

(*a*) Reduction to ammonia by nascent hydrogen.

Prepare 200^{cc} of a solution of caustic soda free from ammonia by adding cautiously and in small pieces 4 grams of metallic sodium to 200^{cc} of good distilled water.

Add 200^{cc} of the water to be tested to the same quantity of the caustic soda solution, and into the mixture introduce an excess of aluminum foil. Let stand a number of hours.

Pour the liquid from the undissolved aluminum into the litre flask, add 50^{cc} of the permanganate solution, and distill off 250^{cc}. Nesslerize 50^{cc} as in the determination of the ammonias.

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* Water Analysis, pp. 67-68.

In case a large quantity of nitrates is present, it would be more convenient to Nesslerize 5^{cc}–10^{cc} of the distillate, to which add sufficient distilled water to make 50^{cc}.

From the results herein obtained, deduct the amount of the ammonias; and $\frac{63}{17}$ of the remainder is nitric acid.

(*b*) The phenolsulphonic acid method.

Add 1-10^{cc} of a saturated solution of sodium carbonate to 100^{cc} of the water, and evaporate to dryness on the water-bath. The sodium carbonate prevents loss from the volatilization of free nitric acid. With the dish covered by a watch-glass on account of effervescence, thoroughly moisten the residue with 2^{cc} of the standard phenolsulphonic acid. It is diluted with water, rendered alkaline with ammonia, and poured into a Nessler glass of 100^{cc} capacity. Distilled water is added to the mark. The color is compared with other glasses containing varying amounts of the standard potassium nitrate solution, each containing 5^{cc} of strong ammonia water. Permanent nitrate standards can be kept for some weeks. If there is a high chlorine content in the water, there should be added to each Nessler glass a quantity of the standard sodium chloride solution equal to the amount found in the water.

Reaction:

$$C_6H_3OH(SO_3H)_2 + 3HNO_3 = C_6H_2OH(NO_2)_3 + 2H_2SO_4 + H_2O$$

Ammonia forms yellow ammonium picrate with this trinitro phenol:

$$C_6H_2OH(NO_2)_3 + NH_4OH = C_6H_2ONH_4(NO_2)_3 + H_2O$$

13. To determine the nitrites. The Griess-Ilosvay reaction.

Place 100^{cc} of the water under examination in a Nessler jar, add to it one drop of concentrated hydrochloric acid, 2^{cc} of the sulphanilic acid solution, and 2^{cc} of the solution of naphthylamine hydrochloride. Mix thoroughly. Cover with a watch-glass and let the jar stand for thirty minutes. Prepare similar Nessler jars with known quantities of the standard nitrite solution, and dilute to the 100^{cc} mark with nitrite-free distilled water, adding the same reagents as were introduced into the first jar. At the expiration of thirty minutes, a comparison of the known with the unknown can be made, and the nitrogen of the nitrite in the water accurately determined.

14. To determine the phosphates.

These are determined by Phipson's method. To a litre of the water add a small quantity of a solution of common alum, a few drops of ammonia, and acidify with acetic acid. Allow the precipitate of aluminum phosphate to settle. Filter, dissolve in nitric acid, and precipitate in the usual way with a solution of ammonium molybdate.

Water may occasionally contain arsenic, barium, manganese, copper, lead, and other substances. For the estimation of these and their significance, the student is referred to the special works on water analysis.

Remarks.

1. Chlorine.

All waters contain a certain "normal" amount of chlorine, usually as sodium chloride, which varies greatly in different localities. The amount is quite high in waters near the sea-coast, and in wells in such localities as Syracuse, N. Y. The time will doubtless come when each state will have a chart of the normal amounts such as has already been worked out for some localities. An excessive amount of chlorine indicates sewage contamination. So a considerable interest always attaches to this determination.

2. Nitrates.

These are more likely to denote the decomposition of animal than of vegetable substances. Stoddart says, "Natural waters can at most obtain but from 1-10 to 2-10 gram of nitrogen as nitrates per imperial gallon (1.43 to 2.86 parts per million), from sources other than animal matter, and practically the whole of the nitrogen of sewage may be oxidized into nitric acid without diminishing the risk involved in drinking it."

3. Nitrites.

Mallet has reported upon the presence of nitrites in eighteen "natural waters believed to be of good, wholesome character," collected from a great variety of sources. His determinations show an average of 0.0135 part nitrogen as nitrites per million parts of water. Mason says his experience has been that the average amount of nitrites found in good waters is very much less than the value given by Mallet. Considerable quantity of nitrites is sometimes found in deep well and spring waters. They result from the reduction of nitrates by ferrous salts or by organic matter which may have been imbedded for ages.

4. Phosphates.

These are usually found only in small traces in good waters. If in considerable quantity, they indicate contamination, although there are known exceptions to the rule.

5. As an aid to determining the purity of a drinking water, the source of the water and its surroundings should be as carefully and thoroughly investigated as circumstances may permit. All available data should be considered in forming a judgment as to the potability of a given water.

The apparatus, chemicals, and minerals necessary for this course can be obtained of the usual dealers. For the most part, the articles will be found comparatively inexpensive.

PART V

APPENDIX

PART V.

APPENDIX.

Equations that express some of the more complicated reactions.

SIDERITE.

(Page 36.)

Total iron, FeO and Fe_2O_3.
$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$.
$FeCO_3 + 2HCl = FeCl_2 + H_2O + CO_2$.
$FeCl_2 + HCl + HNO_3 = FeCl_3 + H_2O + NO_2$.
$2FeCl_3 + 3BaCO_3 = Fe_2(CO_3)_3 + 3BaCl_2$.
$Fe_2(CO_3)_3 + 6HCl = 2FeCl_3 + 3BaCl_2$.
$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.
$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$.
$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$.
MnO.
$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.
$MnCO_3 + 2HCl = MnCl_2 + H_2O + CO_2$.
$MnCl_2 + (NH_4)_2S = MnS + 2NH_4Cl$.
$MnS + 2HCl = MnCl_2 + H_2S$.
$MnCl_2 + Na_2CO_3 = MnCO_3 + 2NaCl$.
$MnCO_3 = MnO + CO_2$.
$3MnO + O = Mn_3O_4$.

GERMAN SILVER.

(Page 48.)

Fe. $3Fe + 8HNO_3 = 3Fe(NO_3)_2 + 4H_2O + 2NO$.
$Fe(NO_3)_2 + 2HNO_3 = Fe(NO_3)_3 + H_2O + NO_2$.

$2Fe(NO_3)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6HNO_3$.

$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S$.

$2FeSO_4 + H_2SO_4 + 2HNO_3 = Fe_2(SO_4)_3 + 2H_2O + 2NO_2$.

$3C_2H_4(COONa)_2 + Fe_2(SO_4)_3 = Fe_2(C_2H_4)_3(COO)_6$* $+ 3Na_2SO_4$.

The ferric succinate heated becomes $Fe_2O_3 + CO_2 + H_2O$.

Zn. $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO$.

$Zn(NO_3)_2 + H_2SO_4 = ZnSO_4 + 2HNO_3$.

$ZnSO_4 + Na_2CO_3 = ZnCO_3 + Na_2SO_4$.

$HCN + KOH = KCN + H_2O$.

$ZnCO_3 + 2KCN = Zn(CN)_2 + K_2CO_3$.

$Zn(CN)_2 + K_2S = ZnS + 2KCN$.

$ZnS + 2HCl = ZnCl_2 + H_2S$.

$ZnCl_2 + Na_2CO_3 = ZnCO_3 + 2NaCl$.

$ZnCO_3 = ZnO + CO_2$.

SMALTITE.

(Page 52.)

As.

$CoAs_2 + 6HNO_3 = Co(NO_3)_2 + 2H_3AsO_4 + 4NO$.

$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$.

$As_2S_5 + 3K_2S = 2K_3AsS_4$.

$K_3AsS_4 + 40KOH + 32Cl = 4K_2SO_4 + 32KCl + 20H_2O + \underbrace{K_3AsO_4}_{\text{Pot. arsenate.}}$

The excess of KOH and Cl becomes

$2KOH + 2Cl = KClO$† $+ KCl + H_2O$.

$3KClO = KClO_3 + 2KCl$.

Adding dilute HCl.

$2HCl + KClO = KCl + 2Cl + H_2O$. The hypochlorite and also the potassium carbonate are decomposed. The carbonate is formed by the action of CO_2 of the atmosphere upon the caustic potash. It is also necessary to add Conc. HCl to decompose the $KClO_3$, as follows:

---

* Ferric succinate.

† Pot. hypochlorite.

$KClO_3 + 6HCl = KCl + 6Cl + 3H_2O$.
$K_3AsO_4 + 3HCl = H_3AsO_4 + 3KCl$.
$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$.
Co.

$Co(NO_3)_2 + 2KOH = Co(OH)_2 + 2KNO_3$. KOH and HCN are added until the double salt potassium cobalto cyanide, $Co(CN)_2$, 4KCN is formed. This double salt may be expressed in another way: $K_4Co(CN)_6$

$$2K_4CO(CN)_6 + O + H_2O = 2KOH + \underbrace{2K_3Co(CN)_6}_{\text{Pot. cobalti cyanide.}}.$$

Note the change of valence.

Adding dilute H_2SO_4, there results, $K_3Co(CN)_6 + 3H_2SO_4 = 3HKSO_4 + H_3Co(CN)_6$. Adding concentrated sulphuric acid completes the foregoing reaction, and reacts still further.

$2H_3Co(CN)_6 + 19H_2SO_4 = 2CoSO_4 + 12CO + 12N + 17SO_2 + 22H_2O$.

Heating to dryness changes the $HKSO_4$ which is formed, as follows:

$2HKSO_4 = K_2S_2O_7 + H_2O$.
$CoSO_4 + 2KOH = Co(OH)_2 + K_2SO_4$.
$Co(OH)_2 = CoO + H_2O$.

PHOSPHORITE.

(Page 66.)

P_2O_5.
$Ca_3(PO_4)_2 + 6HNO_3 = 3Ca(NO_3)_2 + 2H_3PO_4$.
$Sn + 4HNO_3 = Sn(OH)_4 + 4NO_2$.
$4H_3PO_4 + 3Sn(OH)_4 = Sn_3(PO_4)_4 + 12H_2O$.

$$\left\{\begin{array}{l} Sn_3(PO_4)_4 + 6KOH + 3H_2O = 3K_2SnO_3 + 4H_3PO_4. \\ H_3PO_4 + 3KOH = K_3PO_4 + 3H_2O. \end{array}\right.$$

$K_2SnO_3 + 3H_2SO_4 = K_2SO_4 + Sn(SO_4)_2 + 3H_2O$.
$2K_3PO_4 + 3H_2SO_4 = 3K_2SO_4 + 2H_3PO_4$.
$Sn(SO_4)_2 + 2H_2S = SnS_2 + 2H_2SO_4$.

Fluorine.

The method outlined in the text was devised by Berzeli

$CaF_2 + Na_2CO_3 = CaCO_3 + 2NaF$.
$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$.
$Na_2SiO_3 + (NH_4)_2CO_3 = H_2SiO_3 + Na_2CO_3 + 2NH_3$.

The SiO_2 is not completely precipitated, therefore zinc sulphate dissolved in ammonia is added.

$Na_2SiO_3 + ZnSO_4 = Na_2SO_4 + ZnSiO_3$, and at the same time, $2Na_3PO_4 + 3ZnSO_4 = 3Na_2SO_4 + Zn_3(PO_4)_2$.

The phosphoric acid is thus precipitated. On evaporation the excess of $ZnSO_4$ and Na_2CO_3 becomes $ZnCO_3$ and Na_2SO_4.

$2NaF + CaCl_2 = CaF_2 + 2NaCl$. After acidifying the filtrate with acetic acid, $CaCl_2$ precipitates CaF_2 in such a gelatinous condition that filtration is possible only when a small quantity of calcium carbonate is precipitated with it by Na_2CO_3. After ignition, this $CaCO_3$ is dissolved by acetic acid, and the CaF_2 is left in condition to be filtered.

Granite. (Page 72.)

P_2O_5.

$Ca_3(PO_4)_2 + 6HNO_3 = 3Ca(NO_3)_2 + 2H_3PO_4$.

$7H_3PO_4 + 12(NH_4)_6Mo_7O_{24} + 51HNO_3 = 7[(NH_4)_3PO_4 + 12MoO_3 + 6H_2O] + 51NH_4NO_3$.

$7(NH_4)_3PO_4 + 12MoO_3 + 72NH_4OH = 7(NH_4)_3PO_4 + 12(NH_4)_6Mo_7O_{24} + 36\ H_2O$.

The ammonium phosphate is then precipitated with magnesia mixture as usual.

There is a certainty only in the end products of the foregoing equations. It is not known exactly how the substances combine in the original solutions.

The chemically pure hydroplatinic chloride. (Page 83.)

The object of the treatment is to remove the two or three per cent. of iridium that is usually contained in platinum.

$HCl + HNO_3 = Cl + H_2O + NO_2$.

$Ir + 4Cl = IrCl_4$.

$2IrCl_4 + 8NaOH = 2Ir(OH)_3 + 7NaCl + NaClO + H_2O$.

Adding alcohol to the hot liquid,

$NaClO + C_2H_5,OH = NaCl + CH_3,CHO + H_2O$.

$Ir(OH)_3 + 3HCl = IrCl_3 + 3H_2O$.

The iridious chloride is not precipitated by KCl, while the hydroplatinic chloride is precipitated.

$2KCl + H_2PtCl = K_2PtCl_6 = 2KCL, PtCl_4$.

$2KCl, PtCl_4 + 4H = 2KCl + 4HCl + Pt$.

$Pt + 4Cl + 2HCl = H_2PtCl_6$.

The Pettenkofer method of estimating the carbon dioxide in water.

1. The ammonium chloride prevents the precipitation of magnesia by the lime-water. Such precipitation would diminish the alkalinity of the solution and cause an error.

2. The $CaCl_2$ sets free the weakly united (*semi-gebunden*) CO_2, so that it may be determined. Carbon dioxide in a solution containing an alkali carbonate forms the bicarbonate as follows:

$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$.

$2NaHCO_3 + CaCl_2 = 2NaCl + H_2O + CO_2 + CaCO_3$.

3. Why the difference mentioned in the text expresses the CO_2 in 100,000 parts of the water.

Suppose 45 cc. lime-water corresponds to 40 cc. oxalic acid sol., and 100 cc. water and 45 cc. lime-water cor. to 31 cc. oxalic acid sol.

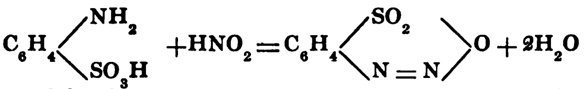
The CO_2 in the water makes a difference of 9 cc. oxalic.

100 cc. water contains 0.009 g. CO_2.

100,000 cc. water contains 9 g. CO_2.

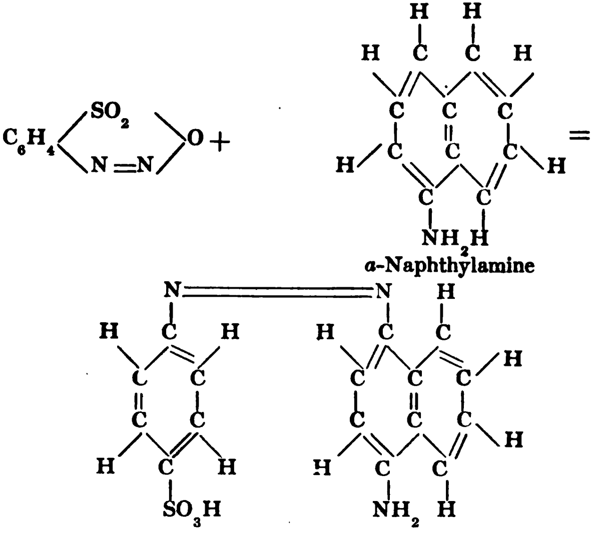
In this case 9 cc. oxalic acid solution less is required because the CO_2 in the water unites with some $Ca(OH)_2$ to form $CaCO_3$. The more CO_2 the water contains, the more $Ca(OH)_2$ would be withdrawn, and the less oxalic solution would be required. 1 cc. of oxalic acid solution corresponds to 0.001 g. CO_2. The 9 cc. difference would correspond to 0.009 g. CO_2, therefore, 100,000 parts of water would contain 9 parts CO_2.

The Griess-Ilosvay reactions for nitrites in water.



$$C_6H_4\left\langle\begin{matrix}NH_2\\SO_3H\end{matrix}\right. + HNO_2 = C_6H_4\left\langle\begin{matrix}SO_2\\N=N\end{matrix}\right\rangle O + 2H_2O$$

Sulphanilic Acid. P. Diazobenzene sulphonic anhydride.



a-Naphthylamine

a-Azo amino naphthylic para benzene sulphonic acid. The substance which is of a pink color.

Permanent standards. Where many determinations of ammonia are made, it is convenient to have permanent standards. These are prepared as follows:

a. Platinum solution. Two grams of potassium platinic chloride are dissolved in a little distilled water, 100 cc. concentrated hydrochloric acid are added and sufficient water to make a litre.

b. Cobalt solution. Twelve grams of cobaltous chloride, $CoCl_2$, $6H_2O$ are dissolved in a little distilled water, 100 cc. concentrated hydrochloric acid are added and water to make a litre.

Standards of twelve different concentrations are conveniently used, made by placing varying amounts of the two solutions in 50 cc. Nessler jars, and diluting to the mark with distilled water.

Equivalent volume of the Weaker Ammonium Chloride Solution	Platinum Solution cc.	Cobalt Solution cc.
0.0	1.2.	0.0
0.5	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	17.3	4.5
3.5	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7

Corks should be inserted in the Nessler glasses to keep the solutions free from dust.

Procedure:—To 50 cc. of the distillate, add 2 cc. of Nessler solution. Allow this to stand, corked, for ten minutes, and then compare with the permanent standards. Suppose this corresponds to the third number in the table, or 0.7. This number multiplied by 8 and again by .01 = 0.056, the amount of ammonia in 1,000,000 parts of the water.

Figure 5 shows an apparatus for reading Nesslerized ammonia tubes. The twelve standards are in the tubes

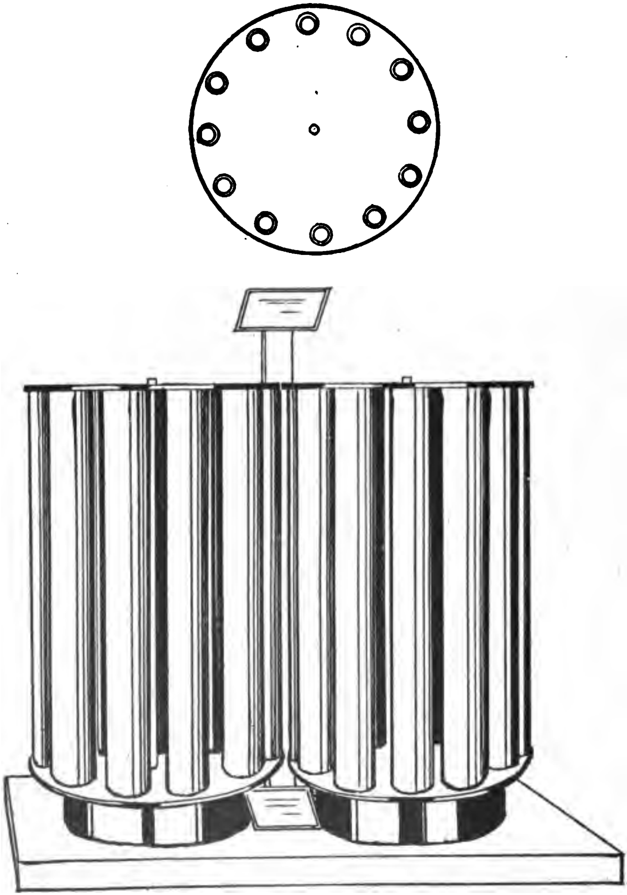


Fig. 5.

on the left, and the free and albuminoid ammonias are in tubes on the right. The two sets can be rotated, until the colors on the left and right correspond. The amount of ammonia per million parts of water that each tube corresponds to can be pasted on the outward metal cylinder. The apparatus may be used for determining the amount of nitrate in drinking water, when it is reduced to ammonia by nascent hydrogen.

To find the weight of a given volume of gas.

$$P = \frac{W \times V \times (B - f)}{760 \times (1 + 0.00367\ t)}$$

W = Weight of a cubic centimetre of the gas.

V = Volume of the gas in cubic centimetres.

B = The height of the barometer in millimetres.

f = The tension of water vapor for the temperature t, found in table 2.

.00367 = The coefficient of expansion of gas for each degree Celsius.

THE WEIGHT OF A LITRE OF DIFFERENT GASES UNDER NORMAL CONDITIONS, AND THE DENSITIES REFERRED TO AIR.

ACCORDING TO LANDOLT AND BOERNSTEIN.
PHYSICAL-CHEMICAL TABLES.

	Formula.	Weight of 1 litre in Grams.	Density.
Acetylene	C_2H_2	1.16143	0.89820
Air	—	1.29305	1
Ammonia	NH_3	0.76148	0.58890
Bromine	Br_2	7.14115	5.52271
Butane	C_4H_{10}	2.59142	2.00411
Butylene	C_4H_8	2.50190	1.93488
Carbon dioxide . . .	CO_2	1.96503	1.51968
Carbon monoxide . .	CO	1.25050	0.96709
Chlorine	Cl_2	3.16696	2.44921
Cyanogen	C_2N_2	2.32630	1.79907
Ethane	C_2H_6	1.34047	1.03667
Ethylene	C_2H_4	1.25095	0.96744
Hydrobromic acid . .	HBr	3.61534	2.79597
Hydrochloric acid . .	HCl	1.62824	1.25922
Hydrofluoric acid . .	HF	0.89451	0.69178
Hydriodic acid . . .	HI	5.70972	4.41570
Hydrogen	H_2	0.08952	0.06923
Methane	CH_4	0.71502	0.55297
Nitrogen	N_2	1.25440	0.97010
Nitrous oxide	N_2O	1.96892	1.52269
Nitric oxide	NO	1.34172	1.03764
Oxygen	O_2	1.42908	1.10521
Propane	C_3H_8	1.96597	1.52041
Sulphur dioxide . . .	SO_2	2.86146	2.21295
Sulphuretted hydrogen	H_2S	1.52189	1.17697

TENSION OF WATER VAPOR.

FROM 0° TO 35 ° C.

Bunsen gasometrische Methoden. 2d Ed. Page 357.

0 Cels.	Tension in Millimetres	0 Cels.	Tension in Millimetres.	0 Cels.	Tension in Millimetres.	0 Cels.	Tension in Millimetres.
0.0	4.600	9.0	8.574	18.0	15.357	27.0	26.505
+0.5	4.767	9.5	8.865	18.5	15.845	27.5	27.294
1.0	4.940	10.0	9.165	19.0	16.346	28.0	28.101
1.5	5.118	10.5	9.474	19.5	16.861	28.5	28.931
2.0	5.302	11.0	9.792	20.0	17.391	29.0	29.782
2.5	5.491	11.5	10.120	20.5	17.935	29.5	30.654
3.0	5.687	12.0	10.457	21.0	18.495	30.0	31.548
3.5	5.889	12.5	10.804	21.5	19.069	30.5	32.463
4.0	6.097	13.0	11.162	22.0	19.659	31.0	33.405
4.5	6.313	13.5	11.530	22.5	20.265	31.5	34.368
5.0	6.534	14.0	11.908	23.0	20.888	32.0	35.359
5.5	6.763	14.5	12.298	23.5	21.528	32.5	36.370
6.0	6.998	15.0	12.699	24.0	22.184	33.0	37.410
6.5	7.242	15.5	13.112	24.5	22.858	33.5	38.473
7.0	7.492	16.0	13.536	25.0	23.550	34.0	39.565
7.5	7.751	16.5	13.972	25.5	24.261	34.5	40.680
8.0	8.017	17.0	14.421	26.0	24.988	35.0	41.827
8.5	8.291	17.5	14.882	26.5	25.738		

INTERNATIONAL ATOMIC WEIGHTS, 1915

NAME	SYMBOL	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC WEIGHT
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79 92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31 04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorine	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52 0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.07
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

INDEX.

Acidimetry, 108
Alkalimetry, 107
Alkalis, determination, 78, 86
Alumina, determination, 35, 40, 70, 77, 123
Ammonia, albuminoid, determination, 126
Ammonia, free, determination, 126
Ammonium chloride solutions, 120
Ammonium chloride, prevents precipitation of magnesium, 35
Ammonium molybdate solution, preparation, 87
Ammonium zinc sulphate, preparation, 67
Analysis, repetition, 13
Antimony, determination, 60
Appendix, 135
Arsenic, determination, 53, 62
Atomic weights, 147

Balance, care of, 3
Balance, sensitiveness, 3
Balance, support, 3
Barium, determination, 28
Barium chloride, analysis, 28
Barium chloride, decinormal solution, 119
Barium sulphate, treatment, 26
Basic acetate method with iron and alumina, 40
Berzelius-Bunsen method with ferric iron, 39
Bettel's method for titanium, 72
Bismuth, determination, 59
Bumping, avoidance, 11
Burettes, 92
Burettes, calibration, 93

Calcium oxide, determination, 29, 33, 38, 44, 64, 71, 78, 123
Carbon dioxide, determination, 31, 32, 36, 46, 53, 66, 72, 125
Carefulness, 12
Caustic potash, pure, preparation, 20
Caustic soda solution, preparation, 107, 127
Chalcopyrite, analysis, 41
Chalcopyrite, composition, 41
Chlorine, determination, 28, 68, 113, 125
Chlorine in bleaching powder, 113
Chlorine, significance in water, 130
Chromic oxide, determination, 23
Cobalt, determination, 57, 64
Cobalt solution, 141
Cooke, J. P., method for ferrous iron, 84
Copper, determination, 19, 43, 49, 59, 63
Copper sulphate, analysis, 27

Copper sulphate, purification, 27
Crucibles, manner of preparing, 8

Desiccators, 10
Dolomite, analysis, 32
Dolomite, composition, 32
Dolomite, result of analysis, 33
Dolomite, separation of iron and alumina, 34
Drinking water, analysis, 119

Evaporation, 11

Fahlerz, analysis, 59
Fahlerz, composition, 59
Ferric oxide, determination, 39, 97, 98, 123
Ferrous oxide, determination, 32, 39, 82, 84, 98
Filter ashes, to determine weight, 18
Filtering, 6
Filter papers, folding the, 6
Filter papers, preparation, 17
Filter papers, to dry to constant weight, 55
Filter papers, to remove inorganic matter, 17
Filtrate, to test, 7
Fluorine, determination, 66

Gases, weight of a litre, 145
German silver, analysis, 48
German silver, composition, 48
German silver, reactions, 135
German silver, result of analysis, 52
Gooch crucible, 22
Granite, analysis, 72
Granite, composition, 72
Granite, preparation of powder, 72
Granite, reactions, 138
Gravimetric analysis, 17
Gravimetric analysis defined, 17
Griess-Ilosvay reactions, 129, 140

Haematite, the iron by permanganate, 98
Hydrochloric acid, normal solution, 106
Hydrogen sulphide, determination, 110

Iceland spar, analysis, 28
Iceland spar, composition, 28
Iceland spar, result of analysis, 31
Igniting the precipitate, 9
Indicators, 91
Introduction, 3
Iodimetry, 108
Iodine, pure, preparation, 109
Iodine solution, preparation, 108
Iodine solution, to determine value, 110
Iron, determination, 36, 40, 44, 49, 56, 64, 70, 77, 82, 123

Lead, determination, 42, 48, 53, 63
Liebig's method for hydrocyanic acid, 105
Liebig's method for nickel, 56
Lime-water, preparation, 119

Limonite, the iron by permanganate, 97
Lithium, determination, 123, 124
Litmus solution, preparation, 107

Magnesia mixture, preparation, 46
Magnesium oxide, determination, 25, 33, 39, 44, 59, 64, 71, 78, 123, 124
Magnesium sulphate, analysis, 24
Magnesium sulphate, result of analysis, 26
Magnetite, composition, 98
Magnetite, the iron by permanganate, 98
Manganese dioxide, analysis, 98, 113
Manganese oxide, determination of, 38, 64
Manganese sulphate in permanganate titrations, 101
Marguerite's method of standardizing, 100
Mercuric oxide, dry, preparation, 41
Mercury, determination, 64
Mineral analysis, preparation of material, 28
Mitscherlich method for ferrous iron, 82
Molybdenum, determination, 76
Morse, Professor H. N., 94

Naphthylamine hydrochloride, 121
Nessler reagent, preparation, 120
Nickel, determination, 51, 56, 64
Nickel hydroxide, washing, 52
Nitrates, determination, 127, 128
Nitrates, significance in water, 130
Nitrites, determination, 129
Nitrites, significance in water, 131
Normal solution, caustic soda, preparation, 107
Normal solution, hydrochloric acid, preparation, 106
Normal solution, Mohr's definition, 103

Oxalic acid solution, preparation, 120
Oxidizing agents, 94

Permanent standards, 140
Permanganate alkali solution, 120
Permanganate titrations, reactions, 95
Pettenkofer's method, carbon dioxide, 125, 139
Phenol sulphonic acid, preparation, 122
Phosphates, determination in water, 129
Phosphates, significance in water, 131
Phosphoric acid, determination, 46, 69, 73
Phosphorite (Apatite), analysis, 66
Phosphorite, composition of, 66
Phosphorite, reactions, 137
Platinic chloride, preparation, 83
Platinic chloride, reactions, 138

Platinum, care of, 12
Platinum, removing stains, 12
Platinum solution, 141
Potassium, determination, 22, 78, 123, 124
Potassium bichromate, analysis, 22
Potassium bichromate, reactions, 102
Potassium bichromate titrations, 102
Potassium bichromate, to determine its purity, 114
Potassium bromide, analysis, 112
Potassium chromate, neutral solution, 119
Potassium iodide, analysis, 111
Potassium nitrate, standard solution, 122
Potassium nitrate, to determine its purity, 99
Potassium permanganate titrations, 94
Potassium sulphide, preparation, 51
Precipitates, filtering and washing, 6
Precipitates, heating and igniting, 8
Precipitates, how obtained, 5
Precipitates, manner of washing, 7
Precipitates, removal from sides of beaker, 7
Precipitates, to dry, 8
Precipitates, to protect from dust, 8
Precipitates, transference to filter, 6

Reactions, 18
Records, 13
Reduction with hydrogen sulphide, 101

Siderite, analysis, 36
Siderite, composition, 36
Siderite, determination of its iron, 96
Siderite, reactions, 135
Silica, determination, 29, 32, 33, 34, 36, 42, 53, 63, 68, 74, 122
Silver chloride, removal from crucible, 20
Silver coin, analysis, 18
Silver coin, composition, 18
Silver coin, result of analysis, 21
Silver, determination of, 19, 63
Silver halides by Gooch method, 22
Silver, metallic, changed to chloride, 21
Silver nitrate titrations, 103
Silver nitrate, to prepare decinormal solution, 103
Smaltite, analysis, 52
Smaltite, composition, 52
Smith, J. Lawrence, method for alkalis, 86
Sodium carbonate, dry, preparation, 41
Sodium chloride, pure, preparation of, 104
Sodium, determination, 123, 124
Sodium nitrite, standard solution, 121
Sodium oxide, determination, 81
Sodium phosphate, analysis, 46
Sodium phosphate, result of analysis, 48

Sodium thiosulphate, analysis, 111
Solid matter, determination in water, 122
Solutions, to concentrate, 11
Starch solution, preparation, 109
Sulphanilic acid, to prepare solution, 121
Sulphate, determination, 25, 27, 35, 125
Sulphur, determination, 41, 53
Sulphuretted hydrogen, analysis, 110
Sulphurous acid solution, preparation, 109

Tin, determination, 19, 48
Titanium, determination, 72
Titration with potassium bichromate solution, 102
Titration with potassium permanganate solution, 94
Titration with silver nitrate solution, 103

Vacuum pump, 7
Volumetric analysis, definition, 91
Volumetric analysis, advantage of, 91

Water, analysis, 119, 122
Water, determination of, 24, 27, 28, 47, 65, 71, 83
Water, distilled, 7
Water, internal friction of, 7
Water, vapor tension, 146
Weighing, deliquescent substances, 10
Weighing, directions for, 4
Weighing substances for analysis, 5

Zinc, determination, 50, 58, 64